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JOURNAL

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THE CHEMICAL SOCIETY.

I.—*On Namaqualite.*

By Professor CHURCH, M.A.

(Read November 18th, 1869.)

Mr. J. R. GREGORY lately brought from Namaqualand, South Africa, some small specimens of an apparently new copper mineral. He directed my attention to the substance as worthy of investigation. My results are here given in a condensed form.

Namaqualite occurs in thin layers of silky fibres which are true crystals, though their minute size and the general absence of distinct terminations renders it impossible to ascertain the system to which they belong. The layers alternate with irregular bands of a kind of chrysocolla, and are sparingly mixed with small crystals of magnesia mica. The aspect of namaqualite resembles that of chrysolite, but its colour is pale blue, with a silky lustre. Its hardness is 2·5, and its density 2·49. Isolated crystals appear transparent under the microscope. In the closed tube it gives off much water when heated, becoming black.

For analysis, the mineral was coarsely crushed, and the homogeneous fragments carefully picked out under the microscope. The powdered selected pieces lost nothing in weight, either over sulphuric acid in vacuo, or at 100°. The several samples, however, were always submitted to the temperature of 100° before analysis. The following results were obtained with different specimens. Unfortunately, the quantities em-

ployed were small on account of the present rarity of the mineral. I ought to state that the alumina found contained some ferric oxide; how much I could not successfully determine.

ANALYSES OF NAMAQUALITE.

Analysis.	Substance taken.	H_2O.	CuO.	Al_2O_3.	CaO.	$P_2Mg_2O_7$.	SiO_2.
I.	·098	0·315	—	—	—	—	—
II.	·113	·037	—	·017	—	·0095	—
III.	·257	·082	·116	—	—	—	—
IV.	·174	·055	·0772	·027	·0035	·0165	—
V.	·111	—	—	—	—	—	·0025

The foregoing results, translated into percentages, are as follow:—

	I.	II.	III.	IV.	V.
H_2O	32·14	32·74	31·91	32·75	—
CuO	—	—	45·09	44·38	—
Al_2O_3.....	—	15·04	—	15·52	—
CaO	—	—	—	2·01	—
MgO	—	3·01	—	3·42	—
SiO_2	—	—	—	—	2·25

The mean percentages deduced from these numbers are :—

H_2O	32·38
CuO	44·74
Al_2O_3	15·29
CaO	2·01
MgO	3·42
SiO_2	2·25
	100·09

If we exclude the silica as an intruding substance, while we regard the lime and magnesia as replacing a small part of the cupric oxide in this mineral, we may, I think, reasonably regard it as a compound of 4 molecules of cupric hydrate, 1 molecule of aluminium hydrate, and 11 molecules of water. The oxygen-ratio between the protoxides, the aluminium oxide, and the water is 4 : 3 : 11 nearly, and corresponds to such a view.

The suggested formula demands the following percentages (for comparison I have placed the mean experimental results in juxta-position) :—

			Theory, $4CuH_2O_2.Al_2H_6O_6.4$ aq.	Experiment.
$4CuO$.....	79·5 × 4 = 318.....		51·37	44·74
Al_2O_3.....	103 = 103.....		16·64	15·29
$11H_2O$	18 × 11 = 198.....		31·99	32·38
			100·00	

This mineral belongs to the rare class of hydrous oxides in which a protoxide and sesquioxide are united. Hydrotalcite ($Al_2H_6O_6.6MgH_2O_2.6aq.$) and pyroaurite ($Fe_2H_6O_6.6MgH_2O_2.6aq.$) seem to be its nearest allies. The fact that it is crystallised as well as definite and constant in composition, demands for it specific rank.

I am indebted to Mr. J. R. Gregory, not only for the several specimens of namaqualite which I have examined, but also for pointing out the novelty and interest which would probably belong to a careful analysis of the mineral.

My thanks are due to my assistant, Mr. E. Kinch, for the care and skill with which he has executed much of the foregoing analytical work.

II.—*Chemical Researches on New and Rare Cornish Minerals.*

By Professor CHURCH, M.A.

(Read November 18th, 1869.)

No. 6, *Hisingerite.*

LAST summer I obtained from Mr. Talling, of Lostwithiel, some specimens of a dark brown, amorphous mineral which he had recently found, and which for some time appears to have been mistaken for beraunite. I have noted the occurrence of the same brown substance upon a specimen of tamarite from Wheal Gorland, in my possession.

Qualitative analysis showed the mineral to consist of ferric oxide, silica, and water, with traces of magnesia, and, rarely, of ferrous oxide.

The chemical and physical characters of this Cornish mineral approach those of hisingerite or its varieties. Unwilling to increase unnecessarily the number of mineral species, I shall provisionally describe it as hisingerite.

The following are the chief characters of the supposed hisingerite:—Amorphous, reniform, fissured, dark brown. Streak pale rust brown (in some specimens, olive brown). Fragile; fracture irregular conchoïdal. Hardness 2·75; density 1·74. Before blowpipe in closed tube, much water, having faint permanent acid reaction. On charcoal, decrepitates and becomes black. Fuses with difficulty in outer flame to a red brown bead. Boiled in acids, leaves a silicious skeleton.

The Cornish hisingerite is very hygroscopic: a specimen lost 28·65 per cent. in vacuo over sulphuric acid. But when the powdered mineral, thus freed from accidental moisture, was heated to 100°, its further diminution in weight amounted to no more than 0·54 per cent. In the following analysis the substance was therefore dried at 100° till constant:—

Analysis.	Substance taken.	Fe_2O_3.	SiO_2.	H_2O.
I.	·195	—	·07	·019
II.	·136	·072	·0495	·0155
III.	·1345	—	—	·014

Reduced into mean percentages, these results stand thus:—

Fe_2O_3	52·94
SiO_2	36·14
H_2O	10·49
	99·57

The mineral was found to contain 0·82 per cent. of P_2O_5 and traces of magnesia. In the above iron determination the P_2O_5 was excluded, since the permanganate process was used to control the result of the direct precipitation of the ferric oxide. The oxygen ratio between the ferric oxide, the silica, and the water is 15 : 18 : 16 or 5 : 6 : 5 nearly. But the ratio 3 : 4 : 2 is not only simpler, but probably represents the true relation

of the constituents of the mineral more exactly. The corresponding formula is $Fe_2O_3.2SiO_2.2aq$. The percentages demanded by this expression, together with those deduced from the before-mentioned ratio and from the experiments, are here compared :—

	Theory.		
	I. $Fe_2O_3.2SiO_2.2H_2O$.	II. $5Fe_2O_3.9SiO_2.8H_2O$.	Experiment.
Fe_2O_3	50·63	53·74	52·94
SiO_2	37·98	36·58	36·14
H_2O	11·39	9·68	10·49
	100·00	100·00	99·57

The chief discrepancy between Theory No. I and experiment lies in the percentages of ferric oxide, which is 2·31 per cent. higher than it should be. This arises partly from the presence in the specimen analysed of traces of ferrous oxide, and partly from the difficulty of separating the hæmatitic matrix from the portion of the mineral taken for examination. Thus not only has the iron percentage been raised, but the silica and water percentages have been reduced below those required by the formula $Fe_2O_3.2SiO_2.2H_2O$.

Owing chiefly to the imperfect methods of drying minerals for analysis, the analyses of hisingerite previously made are not easily interpreted into a definite formula, the percentage of water found by different chemists varying between 11·54 and 22·83. If the Cornish mineral now under discussion be rightly assigned to hisingerite, its analysis may throw some light on the constitution of that species, and, at any rate, introduces a mineral new to Britain. It is instructive to note, in this connection, that if we correct the percentages of water found in the analyses of hisingerite from various localities, by deducting, where known, the proportion lost at 100°, the mean percentage result approaches very closely to that obtained in the analysis of the Cornish specimens. But it should be stated, on the other side of the question, that the density of the Cornish mineral in its natural condition is only 1·74, while that of hisingerite is about 2·5, and that there are also further differences, both chemical and physical, but generally minute, between the English and foreign specimens of the mineral.

III. — *On Chloranil and Bromanil.* No. II.

By John Stenhouse, LL.D., F.R.S., &c.

Chloranil.

In addition to the reactions already known, by which Chloranil has been produced, I may mention that when phenol was subjected to the long-continued action of chloride of iodine in presence of water, it yielded a brown crystalline mass, from which chloranil was obtained equal to half the weight of the phenol originally employed. I likewise found that when the red oil,* obtained in the ordinary process for preparing chloranil, was dissolved in a very dilute boiling solution of caustic soda, along with a sufficient quantity of potassic chlorate, and hydrochloric acid then added, it also yielded a small quantity of crystalline scales, which proved to be a mixture of chloranil and terchlorquinone.

Although the first of these processes is theoretically interesting, neither of them is adapted for the economical preparation of chloranil in quantity.

When the above mentioned red oil was digested for some time with nitric acid, sp. gr. 1·36, a considerable evolution of red fumes took place, and chloropicrin distilled over into the receiver. The bright yellow residue remaining in the retort was found to be chloranil.

Chloranilic Acid.

The following modification of the process, described by Graebe,† I have found to be the best for the preparation of this acid. Five parts of chloranil, moistened with alcohol, were added to a cold solution containing six parts of potassic hydrate in 150 of water; the whole was allowed to stand for several hours, with occasional stirring, until the yellow chloranil scales had disappeared, and a portion of the potassium salt had crystallised out in dark red needles. From 10 to 15 parts of chloride of sodium were then added, which completely precipi-

* Chem. Soc. Jour., 1868, p. 142.

† Ann. Ch. Pharm, cxlvi, p. 31.

tated the chloranilic salt, as it is quite insoluble in a cold solution containing 8 to 10 per cent. of sodic chloride. After standing some time, the precipitate was collected, and freed from the dark brown mother-liquor by washing well with a solution of common salt. One or two solutions in boiling water and precipitations by common salt, and a final crystallisation from distilled water, rendered the chloranilic salt quite pure. It was generally necessary to add a little sodic carbonate each time to the solution, to decompose any chloranilate of magnesium, or calcium, formed from the chlorides of magnesium and calcium usually present in common salt.

The pure chloranilate thus obtained was dissolved in 100 parts of boiling water (about 40 times its weight), and 10 parts of hydrochloric acid added; on cooling, the whole of the chloranilic acid was deposited in bright red shining scales, which were perfectly pure.

By this process chloranil yielded from 65 to 67 per cent. of its weight of pure chloranilic acid, the theoretical quantity being 84·96 per cent.

When caustic soda was substituted for the potassa in the above reaction, much less acid was obtained, as was also the case when the solutions were heated, or when potassic or sodic carbonate was used. Hydrates of calcium and barium, and also magnesia, were found to decompose chloranil, with formation of the corresponding chloranilates.

By far the best method, however, of preparing the alkaline chloranilates in the pure state, was first to make pure chloranilic acid, and then neutralize this with the corresponding alkaline hydrate or carbonate. The sodium salt, when dried at 100° C., was found to lose 12·6 per cent. water; $2H_2O$ require 12·46 per cent.

An analysis was also made of the same salt, dried at 100°, with the following results:—

I. ·334 grm. substance gave ·189 grm. Na_2SO_4.

II. ·379 grm. substance gave ·211 grm. Na_2SO_4.

			I.	II.	Mean.
C_6	72	28·45	—	—	—
Cl_2	71	28·06	—	—	—
Na_2	46	18·19	18·33	18·04	18·19
O_4	64	25·30	—	—	—
	253	100·00			

The sodium salt dried at the ordinary temperature is therefore $C_6Cl_2Na_2O_4 + 2H_2O$. When neutral solutions of chloranilate of sodium are boiled, they are rather rapidly decomposed, with production of a dirty brown substance, which remains in solution; but this does not take place when an excess of sodic carbonate is present, even at temperatures considerably above 100° C.

Chloranilic Ether.

One part of chloranilate of silver was digested with five of ethylic iodide, until the whole of the dark red silver salt was converted into iodide; the excess of iodide of ethyl was distilled off, and the chloranilic ether extracted by boiling alcohol, in which it was tolerably soluble. When well washed with hot water, and crystallised once or twice from spirit, it was quite pure. It is soluble in benzol, light American oil, bisulphide of carbon, and ether, and slightly soluble in boiling water. It crystallises in flattened prisms of a bright red colour, and melts at 107° C. Dried at 100° C., and submitted to analysis, it gave the following results:—

I. ·301 grm. substance gave ·500 grm. carbonic anhydride, and ·108 grm. water.

			I.
C_{10}	120	45·29	45·31
Cl_2	71	26·80	—
H_{10}	10	3·76	3·98
O_4	64	24·15	—
	265	100·00	

The ether, as might be expected, is therefore $C_6Cl_2(C_2H_5)_2O_4$.

Action of Nitric Acid on Chloranilic Acid.—When pure chloranilic acid was warmed with twice its weight of nitric acid, sp. gr. 1·45, a strong reaction ensued, chloropicrin distilled over, and a white crystalline substance remained in the retort, which, on analysis of the lime salt, proved to be oxalic acid.

Action of Chloride of Iodine on Chloranilic Acid.—When a current of chlorine was passed through chloranilic acid suspended in water, the acid very slowly disappeared, so that, even after several days, the greater portion remained unacted on. I was, therefore, induced to try the action of chloride of iodine. Three parts of pure chloranilic acid, about one of iodine, and six of

water, were placed in a flask, and a slow current of chlorine passed through the mixture, which was kept warm, until the chloranilic acid had entirely disappeared, and an oily layer had collected at the bottom of the flask. On cooling, large transparent plates crystallised out of the supernatant liquor, and the insoluble lime-salt of this acid was dried at 100° and analysed.

·540 grm. lime-salt gave ·501 calcic sulphate, which is equivalent to 27·35 per cent. calcium; $\left.\begin{matrix} C_2O_2'' \\ Ca_2 \end{matrix}\right\}O_2 + H_2O$ requires 27·39 per cent. The plates are, therefore, oxalic acid. The heavy oily layer, which has an odour analagous to chloropicrin, I am at present investigating.

Action of Bromine on Chloranilic Acid.—Two parts of chloranilic acid were suspended in 20 parts water, and three parts bromine gradually added, with constant agitation, until the chloranilic acid had completely dissolved, forming a pale yellow solution. On the addition of two parts more bromine, the liquid became warm, effervesced slightly, and after standing 24 hours deposited a white crystalline precipitate. This was collected, well washed with cold water, in which it was quite insoluble, dried at a gentle heat, and crystallised several times from bisulphide of carbon. The substance dried in vacuo gave the following results:—

I. ·396 grm. gave ·124 grm. carbonic anhydride.

II. ·455 grm. gave ·145 grm. carbonic anhydride, and ·009 grm. water.

III. ·432 grm. gave ·778 grm. bromide of silver, and ·221 grm. chloride of silver.

IV. ·361 grm. gave ·646 grm. bromide of silver, and ·181 grm. chloride of silver.

			I.	II.	III.	IV.	Mean.
C_6.....	72·0	8·62	8·54	8·70	—	—	8·62
Br_8	640·0	76·60	—	—	76·63	76·14	76·39
Cl_3	106·5	12·75	—	—	12·66	12·41	12·54
H.....	1·0	·12	—	·22	—	—	·22
O.....	16·0	1·91	—	—	—	—	—
	835·5	100·00					

This corresponds very closely to $C_6Br_8Cl_3HO$, but I abstain from naming it, as at present I have been unable to verify this

formula, and wait, therefore, until the investigation of the corresponding oily chlorine compound mentioned above shall have thrown some light on the subject. The substance is very soluble in bisulphide of carbon, from which it crystallises by slow spontaneous evaporation in very large colourless prisms. It dissolves in alcohol, but is at the same time partially decomposed, as on evaporation of the solution, even at the ordinary temperature, aldehyde is given off, and an oil remains. It dissolves readily in benzol and ether, melts at 79·5° C., and distils unchanged. It is apparently unaltered by boiling sulphuric acid.

Bromanil.

This substance, which I described in 1854,* was prepared by the action of bromine on picric acid, but the quantity obtained was small in proportion to the amount of bromine and picric acid employed, bromopicrin being the chief product. The process, moreover, was a very tedious one.

After making numerous trials to discover a better method of preparation, I found the following to be far the best, as by it bromanil can be obtained nearly as easily as chloranil.

A known quantity of bromine was placed in a flask, with one-third its weight of iodine, and five times its weight of cold water. A good cork, furnished with a long digestion tube, was inserted into the neck of the flask, and a quantity of phenol, equal in weight to one-tenth of the bromine, slowly introduced down the tube; a powerful reaction took place, and the contents of the flask became very hot. The phenol adhering to the sides of the tube was then washed down by five parts more boiling water, and the whole digested for one or two hours at 100° C. When cold, the semi-solid contents of the flask were collected, freed as far as possible from the mother-liquors by means of Bunsen's admirable vacuum filter, and digested once or twice in the cold with bisulphide of carbon, in order to remove the terbromophenic acid formed during the reaction. This left the now tolerably pure bromanil undissolved, as yellow crystalline scales, closely resembling in appearance crude chloranil, which, after being treated once or twice with boiling alcohol, and finally crystallised from purified benzol (16 parts), was obtained in a state of purity.

* Ann. Ch. Pharm., xci, p. 339.

·601 grm. dried at 100° C. gave ·371 grm. carbonic anhydride and 1·014 grm. water.

			I.
C_6	72	16·98	16·84
Br_4	320	75·47	—
O_2	32	7·55	—
	424	100·00	

Bromhydranil.

Although, as I have previously stated,* aqueous solution of sulphurous acid converts bromanil into bromhydranil, there is a considerable loss, owing to the formation of secondary products, and it has a brown colour which is extremely difficult to remove.

I found however that, as in the case of chloranil,† when bromanil was digested with hydriodic acid and phosphorus, it gave the theoretical quantity of colourless bromhydranil $C_6Br_4O_2,H_2$.

Action of Sulphurous Acid on Bromanil.

Terbromhydroquinone.

Although bromhydranil was the principal product obtained in passing sulphurous anhydride through boiling water holding bromanil in suspension, about 17 per cent. was converted into an organic acid, which remained in solution along with the sulphuric and hydrobromic acids formed at the same time. This solution was neutralized with carbonate of lead, and the resulting product submitted to sublimation in a manner precisely similar to that employed in the case of the corresponding chloranil compound.‡ The yield of terbromhydroquinone was, however, very small, the greater portion of the substance undergoing decomposition. Owing to the smallness of the quantity I obtained, I was unable to subject it to analysis; but from the similarity of its reactions and physical properties to those of terchlorhydroquinone, it is undoubtedly the corresponding bromine compound, $C_6Br_3H_3O_2$ terbromhydroquinone.

* Ann. Ch. Pharm, xci, p. 310. † Chem. Soc. Jour., xxi, p. 145.
‡ Chem. Soc. Jour., xxi, p. 146.

Terbromoquinone.

When the above-mentioned solution, obtained by the action of sulphurous acid on bromanil, was concentrated by evaporation, and sulphuric acid and acid chromate of potassium added in excess, a brownish-yellow precipitate was produced, consisting of terbromoquinone, $C_6Br_3HO_2$, which was readily purified by one or two crystallisations from dilute alcohol, in which it is very soluble. Its physical characteristics and chemical properties resemble those of terchlorquinone.

Bromanilic Acid.

This acid was prepared in a precisely similar manner to chloranilic acid, which it resembles very closely in appearance and properties. The action of nitric acid upon it was, as might be expected, similar to that on chloranilic acid, bromopicrin and oxalic acid being the chief products. Alkaline sulphites also produced the corresponding salts of bisulpho-bibrom-hydrochinonic and thiocronic acids $C_6\begin{cases}(HO)_2\\Br_2\\(HSO_3)_2\end{cases}$ and $C_6\begin{cases}HO\\(HSO_3)O.\\(HSO_3)_4\end{cases}$

The action of an aqueous solution of sulphurous acid on bromanilic acid at 100° does not appear, however, to produce the acid corresponding to Koch's hydrochloranilic acid $C_6Cl_2H_4O_4$.

Bromanilphenylamide.

This compound, analogous to the corresponding chlorine body discovered by Hesse,* was best obtained by adding an excess of aniline to bromanil dissolved in hot benzol, and washing the almost black crystalline plates which are formed, with boiling alcohol, in which they are nearly insoluble. Dried at 100° C., they gave the following result:—

·420 grm. substance gave ·357 grm. bromide of silver:—

* Ann. Ch. Pharm, cxiv, p. 303.

			I.
C_{18}	216	48·20	—
H_{12}	12	2·68	—
Br_2	160	35·73	35·56
N_2	28	6·25	—
O_2	32	7·14	—
	448	100·00	

This corresponds to the formula, $\left.\begin{matrix}(C_6H_5)_2\\H_2\\(C_6Br_2O_2)''\end{matrix}\right\}N_2$.

Action of Bromine on Bromanilic Acid.—When three parts by weight of bromine were gradually added, with constant stirring, to one part of bromanilic acid suspended in eight parts of cold water, the bromanilic acid dissolved, forming a transparent deep yellow solution, which at the same time became warm and effervesced slightly. In a short time the clear solution lost its transparency, and, after standing 24 to 48 hours, deposited a large quantity of indistinct crystals, more than equal in weight to the bromanilic acid originally employed (1·25 parts). These were collected, well washed with cold water, in which they were quite insoluble, and crystallised two or three times from pure and dry bisulphide of carbon. They were thus obtained in colourless transparent prisms, which melt at 110°5 C., and are very soluble in ether, bisulphide of carbon, and benzol. They are also soluble in alcohol, but apparently undergo decomposition at the same time. Dried at 100° C., they gave the following results:—

I. ·675 grm. substance gave ·183 grm. carbonic anhydride and ·009 grm. water.

II. ·538 grm. substance gave ·147 grm. carbonic anhydride and ·005 grm. water,

III. ·187 grm. substance gave ·399 grm. bromide of silver.

IV. ·373 grm. substance gave ·797 grm. bromide of silver.

			I.	II.	III.	IV.	Mean.
C_6	72	7·43	7·40	7·45	—	—	7·43
Br_{11}	880	90·82	—	—	90·80	90·93	90·86
H	1	·10	·15	·10	—	—	·12
O	16	1·65	—	—	—	—	—
	969	100·00					

This agrees tolerably well with the formula $C_6Br_{11}HO$.

I cannot conclude this paper without expressing my obligations to Mr. Charles E. Groves for the very efficient assistance he has rendered me in this investigation.

IV.—*On Salts of Acetylinated Ethyl—a new Class of Derivatives of the Ethyl-Series.*

By J. Alfred Wanklyn, Corresponding Member of the Royal Bavarian Academy of Sciences.

(Read November 18, 1869.)

The study of metamorphoses of the products given when metallic sodium acts upon acetic ether, has revealed the existence of a very interesting set of chemical compounds, viz., the salts of a new organic radical, wherein a portion of the hydrogen contained in the alcohol-radical has undergone replacement by acetyl. The following terms are known :—

Acetate of acetylinated ethyl,

$$\left.\begin{matrix} C_2H_4(C_2H_3O) \\ C_2H_3O \end{matrix}\right\} O.$$

Butyrate of acetylinated ethyl,

$$\left.\begin{matrix} C_2H_4(C_2H_3O) \\ C_4H_7O \end{matrix}\right\} O.$$

Caproate of acetylinated ethyl,

$$\left.\begin{matrix} C_2H_4(C_2H_3O) \\ C_6H_{11}O \end{matrix}\right\} O,$$

and by the employment of known methods the series might be indefinitely extended.

The first of these compounds is produced by treating sodium-triacetyl (the new product got by the action of sodium on acetic ether) with acetic acid, whereby acetate of sodium results and the organic product loses an equivalent of sodium, and gains an equivalent of hydrogen. Inasmuch as sodium when existing in its least condensed state, is *triatomic*, it cannot strictly speaking, be *replaced* by an atom of hydrogen, and,

accordingly, sodium-triacetyl does not yield hydrogen-triacetyl, but a compound isomeric with the latter, viz., acetate of acetylinated ethyl, thus :—

$$\left.\begin{matrix} H \\ (C_2H_3O)_3 \end{matrix}\right\} = \overset{\text{Acetate of Acetylinated Ethyl.}}{\left.\begin{matrix} C_2H_4(C_2H_3O) \\ C_2H_3O \end{matrix}\right\} O.}$$

The second compound is produced similarly when sodium-triacetyl is attacked by iodide of ethyl. Instead of ethyl-triacetyl there is butyrate of acetylinated ethyl, thus :—

$$\left.\begin{matrix} C_2H_5 \\ (C_2H_3O)_3 \end{matrix}\right\} = \left.\begin{matrix} C_2H_4(C_2H_3O) \\ C_4H_7O \end{matrix}\right\} O.$$

The third compound is a product of the action of iodide of ethyl on acetate of ethylene-sodium (the isomer of butyrate of soda recently described by me, which yields alcohol and acetate of soda when treated with water) :—

$$2\left.\begin{matrix} C_2H_4Na \\ C_2H_3O \end{matrix}\right\} O + 2C_2H_5I = \overset{\text{Caproate of Acetylinated Ethyl.}}{\left.\begin{matrix} C_2H_4(C_2H_3O) \\ C_6H_{11}O \end{matrix}\right\} O} + C_2H_6O + Na_2I_2.$$

The characteristic property of salts of acetylinated ethyl is that of yielding salts of common ethyl by replacement of the acetyl with hydrogen. This reaction is effected by the employment of ethylate of sodium, thus :—

$$\left.\begin{matrix} C_2H_4Na \\ H \end{matrix}\right\} O + \overset{\text{Butyrate of Acetylinated Ethyl.}}{\left.\begin{matrix} C_2H_4(C_2H_3O) \\ C_4H_7O \end{matrix}\right\} O} = \overset{\text{Butyric Ether.}}{\left.\begin{matrix} C_2H_5 \\ C_4H_7O \end{matrix}\right\} O} + \left.\begin{matrix} C_2H_4Na \\ C_2H_3O \end{matrix}\right\} O.$$

and consists in the exchange of acetyl for hydrogen.

The first and second of these salts of acetylinated ethyl were discovered by Geuther, and the third by Frankland and Duppa; and all three have received other names expressive of the views which these chemists entertained of their constitution.

Besides the reaction with ethylate of sodium, there is a very interesting reaction with baryta water (vide Geuther, Frank-

land, and Duppa) whereby carbonate of baryta, alcohol, and a ketone are produced, thus :—

Butyrate of Acetylinated Ethyl. Ketone. Alcohol.

$$\left.\begin{matrix}Ba\\H_2\end{matrix}\right\} O_2 + \left.\begin{matrix}C_2H_4C_2H_3O\\C_4H_7O\end{matrix}\right\} O = \left.\begin{matrix}C_2H_3O\\C_3H_7\end{matrix}\right\} + C_2H_6O + \left.\begin{matrix}Ba\\CO\end{matrix}\right\} O_2.$$

This reaction may be looked upon as consisting of an exchange of the acetyl and butyryl for two equivalents of hydrogen, derived from the hydrate of baryta, whereby common alcohol is produced; and at the same time the liberated acetyl and butyryl resolve themselves into acetyl-propyl and carbonic oxide, which latter forms carbonate of baryta.

I am engaged in the further investigation of this subject.

8th November, 1869.

V.—*Results of the Analysis of Sea Water, performed on board H.M.S. "Porcupine," July*, 1869.

By John Hunter, M.A., F.C.S., Chemical Assistant, Queen's College, Belfast.

(Read December 2, 1869.)

Comparatively few researches have been carried on with the object of determining the precise amount and nature of the gases which are dissolved in sea water at any great depths below the surface. During the voyage of the "Bonite" in the years 1836–37, samples of sea water were collected, carefully sealed up in flasks, and brought home to be analysed in the laboratory of the College of France. M. Daroudeau,* in a paper read April 30th, 1838, gives the following table of the results of these analyses :—

* Comptes Rendus, t. vi, p. 616.

Date and Place.	Lat.	Long.	Depth in fathoms.	Density 8° to 10° c.	Gas in 100 c.c. of water.	Composition of 100 vols of gas.		
						Carbonic acid.	Nitrogen.	Oxygen.
	° ′	° ′						
Aug. 30th, 1836. Pacific Ocean..	11 8N.	108 50W.	surface	1025·94	2·09	10·51*	83·33	6·16
			70	1027·02	2·23	18·06	71·05	10·09
Mar. 19th, 1837. Bay of Bengal.	11 43N.	87 18 E.	surface	1025·45	1·98	13·97	80·50	5·53
			200	1026·63	3·04	58·15	38·50	3·29
May 10th, 1837. Bay of Bengal.	18 0N.	85 32 E.	surface	1026·11	1·91	13·32	80·34	6·34
			300	1025·86	2·43	30·13	64·15	5·72
July 31st, 1837. Indian Ocean..	24 5S.	52 0E.	surface	1025·77	1·85	12·46	77·70	9·84
			450	1027·39	2 75	34·92	55·23	9·85
Aug. 24th, 1837. Atlantic (South)	30 40 S.	11 47 E.	400	1027·08	2·04	28·82	67·01	4·17

The surface waters were all perfectly transparent, but those collected from a greater depth contained white flocculent particles. The amount of gases held in solution was determined by boiling the water in a flask, and collecting over mercury. In conclusion M. Darondeau states that the total gas in sea water is less near the surface, and the difference in amount increases considerably with the depth. The gas from the deeper water contains more carbonic acid than that from the surface, but this result may have arisen from the decomposition of the flocculent matter previously mentioned.

A few experiments were performed on board the "Bonite" with the following results:—

Pacific Ocean.—September 12th, 1836. Lat., 16° 53′ N.; long., 118° 13′ E.; depth, 380 fathoms. 100 c.c. of the water contain 1·62 c.c. of gases.

Near the Philippine Islands.—November 21st, 1836. Lat., 18° 22′ N.; long., 132° 13′ E.; depth, 300 fathoms. 100 c.c. of the water contain 2·20 c.c. of gases, and 100 c.c. of surface water 2·27 c.c.

Chinese Sea.—November 29th, 1836. Lat., 18° 0′ N.; long., 117° 30′ E.; depth 300 fathoms. 100 c.c. of water contain 3·89 c.c. of gases.

On the coast of Algiers M. Aimé† examined the amount of air contained in sea water from various depths, and concluded

* The carbonic acid in this experiment is uncertain.

† Ann. Chim. Phys, t. 2, p. 535.

that either none, or only a very small quantity, was dissolved. Water from 65 metres gave only from 0·01 to 0·02 of its own volume of air, and from 1249 and 1606 metres, no air, or at least only a few bubbles.

According to Bischof* 10,000 parts by weight of water contain :—

				Observer.
Mediterranean ..	1·1	by weight of	carbonic acid—	Vogel.
Atlantic	2·3	„	„	„
English Channel	2·3	„	„	„
The same	0·77	„	„	Bischof.

Some observations indirectly connected with this subject were made by M. Aimé† on the nature of the gases evolved by marine plants. He found that algæ give off carbonic acid in the dark, and decompose it under the influence of light.

A. Hayes‡ observed that there is more oxygen in surface water than at depths of 100 to 200 feet.

M. Morren§ made a series of experiments during the years 1836–37 on the quantity of gases held in solution by sea water at different seasons of the year. He found that sea water dissolves less air than fresh water, that the latter gives off more in proportion of the contained gases on boiling, and that the carbonic acid constitutes from 9 to 10 per cent. of the gases. If the sea be agitated and exposed to diffuse sunlight, the quantities of oxygen, nitrogen, and carbonic acid are capable of great variation. The oxygen and carbonic acid are in inverse proportion to each other, but the numbers are not identical, and do not form a constant sum. In consequence of the quantity of dissolved gas being much greater on a fine day, we have the oxygen varying from 53·66 to 29·70 per cent., but in ponds and near the sea-shore these limits are increased to 20·78 and 76·04.

The principal determinations of the composition of the air over sea water have been made by M. Lewy,‖ who found, during a voyage to Copenhagen, that the air over the sea varied more than that over the land in proportion to the different

* Chemical and Physical Geology, i, 113.

† Poggendorff's Annal., lx, 404.

‡ Sill. American Jour., 1851, p. 421.

§ Ann. Chim. Phys. [3], xii, 5.

‖ Ann. Chim. Phys. [3], viii, 125, and [3], xxxiv, 5.

solubilities of the gases. Mr. E. T. Thorpe,* in a valuable paper read before the Chemical Society, concludes that the sea does not increase the amount of atmospheric carbonic acid, but that the air over the sea contains proportionally much less carbonic acid than that over the land.

It will be seen from these abstracts that very little has been done towards the investigation of the gases contained in the ocean at any great depth, and that the various experiments made with this object have not by any means yielded identical results.

During the month of July, 1869, I was engaged on board Her Majesty's ship "Porcupine" in analysing some samples of sea water brought up from great depths. The specimens of water were procured by means of a large brass tube attached to the sounding line. This tube had two carefully fitted valves placed in it, one at the upper end, the other below, but both opening upwards, so that, when the instrument was descending, the water flowed freely through it, but on proceeding to draw it up, the pressure of the external water closed the valves, and the sample of the last water which had entered the tube was secured. The method worked perfectly, except when the sounding line came up at a great angle, in which case the valves seemed not to hold in quite so well as when the line was brought up perpendicularly.

Having got the water on board, one portion of about 800 c.c. was placed in a flask, and the gases determined by boiling, according to the method of Dr. Miller. In every case the total gas was divided into two portions, so that duplicate experiments could be obtained. The amount of organic matter in two quantities of water of 250 c.c. each was observed by Dr. Miller's process,† and the specific gravity was taken with great care by means of two or three instruments.

It will be observed that the tables consist principally of two sets of experiments made on waters taken from the bottom and intermediate depths in the same locality. In both of them the bottom water was muddy, and the succeeding specimens quite clear. In the second series, the quantity of dissolved gas was very great, so that on a slight elevation of temperature it began to escape. It is to be regretted that I had not more opportunities of examining surface waters, but this was un-

* Chem. Soc. Jour. [2], v, 199. † Chem. Soc. Jour. [2], iii, 122.

avoidable, as the number of intermediate waters brought up required constant attention, and had to be analysed as soon as possible. With regard to the composition of the gases, the carbonic acid was found in each case to be in greatest quantity at the bottom; it then diminished a certain amount, and remained pretty constant until within about 100 fathoms of the surface, when it diminished still more. The specific gravity of the bottom water is rather less than that of the surface in the first series, while in the second the two are identical. The amount of organic matter is about the same in bottom and surface water. In every case where a specimen of water was brought up, the temperature of the water at that depth was ascertained, and the volumes of the gases in the following tables are reduced to those temperatures and 760 mm.

First Series.

Lat. 47° 39′ 0″, Long. 11° 33′ 0″. July 23rd, 1869.

Depth in fathoms.	Temp. Fahr.	Sp. gr. of bottom and intermediate waters.	Sp. gr. of surface water.	Grms. of oxygen for 250 c.c.	Total gas in 100 c.c.	Composition of 100 vols. of gas.		
						Carbonic acid.	Nitrogen.	Oxygen.
2090	36 4°	1027·3	1027·5	·0016	2 80	35·92	43·54	20·54
1750	36·8	1027·5	..	·0012	—	34·10	45·20	20·70
1500	37·2	1027·5	..	·0017	2·87	31·76	48·04	20·20
1250	37·7	1027 5	..	·0015	2·90	32·00	47·74	20·26
1000	37·8	1027·5	..	·0010	2·60	30·10	49·20	20·70
750	41·4	1027 3	..	·0006	2·20	28·62	49·44	21·94
500	47·8	1027·4	..	·0010	2·80	28·10	49·70	22·20
250	50·5	1027·4	..	·0014	2·70	25·12	52·42	22·46

Second Series.

Lat. 49° 12′ 0″, Long. 12° 52′ 0″. July 27th.

Depth in fathoms.	Temp. Fahr.	Sp. gr. of bottom and intermediate waters.	Sp. gr. of surface water.	Grms of oxygen for 250 c.c. of water.	Total gas in 100 c.c. of water.	Composition of 100 vols. of gas.		
						Carbonic acid.	Oxygen.	Nitrogen.
862	39·8°	1027·5	1027·5	·001	3·5	48·28	17·22	34·50
800	42·0	1027·7	..	·001	2 8	33 75	17 79	48·46
750	42·5	1027·5	..	·0012	2 8	31·92	18 76	49 32
700	43·7	1027 5	..	·0013	—	31 03	19·31	49·66
650	44·4	1027·5	..	—	2·4	30·00	19·80	50·20
600	45·5	1027 5	..	·0005	2·4	28 34	20·14	51 52
550	46·4	1027 5	..	·0009	2·6	29·06	20·70	50·24
500	47 4	1027·5	..	·0014	2·2	27 26	—	—
450	47 6	1027 5	..	·0005	2·8	24·73	22·18	53·09
400	48 5	1027·5	..	·0014	2·5			
350	49·2	1027·3	..	·0015				
300	49·6	1027·3	..	·0018				
250	50 3	1027·3	..	·0019				
200	50 5	1027·3	..	·0017				
50	53·4	1027·3	..	·0014	2·2			

Miscellaneous Experiments.

Date.	Depth.	Lat.	Long.	Temp.	Sp. gr. of bottom water.	Sp. gr of surface water.	Grms. of oxygen for 250 c.c. of water.	Total gas in 100 c.c.	Composition of gas in 100 vols.		
									Carbonic acid.	Nitrogen.	Oxygen.
		° ′	° ′	°							
July 20	74	50 38	9 27	49·5	1026·7	1026·7	·001	—	37·88	45·63	16·49
„ 21	surface	48 50	10 57	—	1027 7	..	·0002	—	3·27	59·63	37·10
„ 21	725	..	..	44·2	1027·6	1027·7	·0024	2·2	24·85	57·02	18·13
„ 23	surface	—	—	—	1027·6	—	·0012	2·4	24·37	50·07	25·56

After the reading of this paper, Mr. McLeod expressed his opinion that, if the absolute quantity of carbonic anhydride or carbonic acid gas in 100 volumes of water had been given, the results would then have been more comparable, and the relation between sea water and ordinary spring water would be shown. The total quantity of gas in 100 volumes

of sea water was much less than he would have expected, and less than is found in ordinary river waters. Thames water, he thought, contained 6 volumes in 100 of the three gases together; while the largest proportion of gas in sea water, according to Mr. Hunter, was only 2·8 in 100. It had been stated that sea water brought from a depth effervesced like soda-water; but that would seem to be almost an impossibility if the quantity of gas obtained was as low as 2·8. It was just possible that, in collecting the water, if there was any pressure in the tube, it would open the upper valve, and allow nearly all the gas to escape; but he (Mr. McLeod) was not in a position to suggest a better apparatus than the one described.

VI.—*Remarks on some Points in the Nomenclature of Salts.*

By H. G. Madan, F.C.S.

(Read December 2nd, 1869.)

It is very much to be regretted that the subject of chemical nomenclature is in such an unsettled state. It seems a real reproach to chemists that scarcely two text-books can be found in which the same system of names is adopted, and that there is hardly a single number of a scientific periodical which does not contain specimens of totally different systems. The extreme difficulty of teaching the science under such conditions is palpable, and it is a poor apology to say that text-books in other branches of science, and even classical text-books (*e.g.*, the Public Schools' Primer as compared with the Eton Grammar) vary greatly in their terminology. But while our ablest chemists appear to agree to differ in their views on the subject, it is hard to suggest what should be done.

The following remarks are offered with great diffidence; they may have, at most, the value of calling more attention to the subject.

The fact observed by chemists is, that certain radicles ("electronegative radicles"), of which chlorine is an example, unite in one, or more than one, definite proportion with certain other radicles ("electropositive radicles"), of which mercury is an example, to form distinct series of compounds or salts.

The problem is—

In the first place to provide a general name for each group of salts which is characterised by containing the same electronegative or electropositive radicle.

In the next place to provide special names which may serve to distinguish the several members of each of the above groups, and to mark the position which each member holds in the series to which it belongs.

The first part of the problem has been solved by general consent (so far as regards the electronegative radicles), as follows:—

The termination of the received name of the electronegative radicle is altered into *-ide*, *-ite*, or *-ate;* the two latter terminations denoting that oxygen is considered to be present in the radicle.

Thus salts containing the chlorine radicle are all called chlorides; salts containing a radicle in which chlorine is associated with a certain amount of oxygen are called chlorites, or chlorates, according to the amount of oxygen they contain.*

It appears unlikely that these terminations will at present be changed.

The second part of the problem has been solved in two ways at least.

1. By adding a prefix, such as *proto-* (or *mono-*), *di-*, *tri-*, *per-*, &c., to the existing generic name for the salts of the electronegative radicle; with it is associated the name of the electropositive radicle, unchanged in form, and used either in the possessive case or adjectivally.

Thus we have "protochloride of mercury" (or mercury protochloride), and "dichloride of mercury" (or mercury dichloride or perchloride), as the respective names for the two combinations which mercury forms with chlorine.

2. By changing the termination of the name of the electropositive radicle into *ic*, or *ous*, the generic name for the salts of the electronegative radicle being left unaltered.

* Some few substances, such as chlorine and sulphur, are found to form, in association with oxygen, more than two radicles. Probably these cases might be best met by making an alteration in the vowel immediately preceding the *-te*, as proposed long ago, by Mr. Griffin. Thus the "perchlorate" radicle might be called "chlorote." The principle of indicating the amount of oxygen in the radicle by a change of a vowel in the name, has been already accepted: there seems no reason why we should not extend it.

Thus we have the names "mercurous chloride" and "mercuric chloride" for the two mercury salts alluded to above.

The first system of nomenclature would seem preferable to the second, since—

a. It requires the minimum of change in existing names. The salts in which chlorine is the electro-negative radicle are all termed chlorides; those in which mercury is the electro-positive radicle are all termed mercury salts. When we wish to denote certain classes of chlorides, we merely add a prefix instead of interfering with the termination of a word.

b. It is the more elastic system of the two. It can be adapted to any series of salts, however extensive, while the *ic* and *ous* system is applicable only to a series consisting of two members. The latter is quite inadequate, for instance, to express the series of nitrogen oxides in such a way as to show their stoïchiometrical relations.*

It is quite true that it is at present rare to find a radicle forming more than two well defined series of salts (except oxides), but what we want is a system which will adapt itself to future discoveries without giving us the trouble of re-constructing it; for the present it would be very convenient to retain the old prefixes *proto-* and *per-;* they are, to say the least, open to no greater objections than *-ous* and *-ic*.† Both indicate merely relative position; both are applicable to series consisting of only two members. But in using proto- and per- we approach most nearly to the usual nomenclature for series consisting of many members, such as the oxides (protoxides, dioxides, trioxides, &c.). There is, moreover, an occasional advantage in being able to speak of a group of substances as "protosalts," in pointing out analogies between them. I do not know that it has been proposed to talk of "ic salts" and "ous salts."

I have some difficulty in seeing the advantage of another practice which is becoming common, viz., that of calling certain

* I am quite aware that there is a very great difference in properties between oxides; between, for instance, the substance represented by the formula N_2O and that represented by the formula N_2O_5. But I cannot help thinking that, if we must choose an alternative, it is preferable that the name should express place in a series, rather than difference in chemical properties. Monatomic mercury and diatomic mercury show, in combination, an equally remarkable contrast of properties; but we do not assign them totally distinct names; at the most we change the termination of the name.

† Perhaps *meio-*, as having a purely relative meaning, would be preferable to proto, cf. "meiocene."

radicles by their Latin names. Why, for instance, should we speak of "*argentic* nitrate," when we obtain (besides oxygen and nitrogen) *silver*, and only silver, from the substance.

We cause hydrogen chloride to act upon excess of *iron*, and we obtain a salt which it is proposed to call *ferrous* chloride.

It might be convenient to distinguish the atom from the molecule by some such distinct name, but, if so, the system should be carried out fully and consistently, or not at all. We must have kalic, natric, stibic, hydrargic, &c.

At present no such consistency is observed, and until we are sufficiently educated to talk of a ferrum saucepan, a cuprum tea-kettle, and an argentum spoon, it would seem preferable to adhere to names in common use. The more sparingly we alter ordinary names against which there is no serious objection, the more acceptable and intelligible will be our nomenclature.

I cannot help thinking that the system of terminology, originally proposed, I believe, by Mr. Harcourt, which is adopted by Professor Roscoe in his "Lessons in Elementary Chemistry," and by Mr. Watts in the new edition of "Fownes' Chemistry," has more of the elements of simplicity, permanency, yet elasticity, than any other. It differs in a comparatively slight degree from the older nomenclature, and hence old chemists have little difficulty in understanding it. It is, so far as one can see, readily adaptable to the progress of chemical discovery, and hence young students may learn it without much risk of having to unlearn it.

It is difficult to see why we should occupy ourselves in criticising the euphony of adjectival terminations (*e.g.*, nickelic, ironous) when our language undoubtedly permits us to dispense with them. No one would speak of a golden watch, a carbonic filter, or a mercuric barometer. It may not be too much to hope that the terminations *-ic* and *-ous* may disappear altogether from our nomenclature, if the purpose they serve can be fulfilled as well or better in other ways.

From the unwieldy names which we are now manufacturing for chemical substances, it would seem possible to endeavour to express too much in a name. What is mainly required appears to be that the name should be a rational and sufficiently distinct mark for the substance to which it is applied.

Professor Attfield thought the chief point about a name should be that it was unalterable. He objected to the use of vowels or of Latin or Greek numerals to express the name of a salt, as our views of the constitution of a substance sometimes change, and when such is the case, it becomes necessary to alter the name.

The President said that Mr. Madan's proposal to revert to the use of such terms as *proto-*, *sesqui-*, and *per-*, in order to designate the place of bodies which differ in their quantity of oxygen and chlorine in a series, implies that the series is known, whereas we are constantly altering our knowledge of such series. These words have been productive of considerable inconvenience and confusion, and he thought the terminations *-ous* and *-ic*, as used by most writers, including Dr. Roscoe and Mr. Watts, were far more convenient. These terminations only denote a kind of difference in the constitution of certain substances: such a difference may be ascertained as a matter of fact. We may find other terms of each series, and a body which was first may become second, but if it contains less oxygen than another, it is correctly distinguished by the termination *-ous* instead of *-ic*. Mr. Madan seems to think it necessary always to retain Latin words if they are used in certain cases. It is held by some persons that a variety of name is in many cases desirable amongst such compounds as Prussian blue, where iron figures in two capacities. He, the President, was not aware that those who advocate the view against which Mr. Madan contends have ever asserted that a Latin name, if used at all, ought universally to be employed; and if English names are insisted on, we should be led into eccentricities not less remarkable than those against which the author contends. Carbon and sulphur are Latin words which, if discarded in favour of the English words, would lead to words like charcoalic oxide and charcoalic acid, and brimstonic acid and brimstonous acid, a change which did not appear to him a very great improvement. It is exceedingly desirable that everybody should bring forward his own impression in the matter, because it is only by general consent that any important system can be established.

Mr. Vernon Harcourt thought the difficulty attaching to the choice of names was inevitable in the present state of chemistry. Either a name must be unsystematic, and merely

express one or two facts about the particular substance, *e.g.*, corrosive sublimate; or, if it be systematic, and expresses a relation between the particular substance and others, it must embody a theory not yet definitely established. With reference to English and Latin names, sulphur has for so long a time been used as an English word, that it is, in reality, no less so than brimstone. The latter, he supposed, was a German word, and sulphur was, originally Latin, but it has now become as thoroughly English as any word in the language. With regard to using *ic* and *ous*, he thought that the terminations *proto* and *per* might equally be said to express facts; and it appeared to him that the objection raised by Mr. Madan, that the terminations *ic* and *ous* served only for two terms of a series, and that this mode of expression cannot be extended in cases where the series extends beyond two terms was a just one. At the same time, he thought that, where there are two parallel series of salts (such as mercurous and mercuric salts, ferrous and ferric salts), it is a great convenience to have these terms, and "ferrous salts" is, perhaps, a better expression than "iron proto-salts," which Mr. Madan recommends as a substitute.

Mr. McLeod remarked that there is a certain excuse for the use of Latin words, for, in almost all cases, they refer to the symbol.

Dr. Odling said that Mr. Madan spoke of the convenience which occasionally attached to the use of such a word as "proto-salts," and to speaking of proto-salts in general. It would be a real advantage if all proto-salts were conceived to have the same constitution; but, as the word proto-salts does not express the constitution any more than -ic and -ous, he could not admit that argument to have any weight in favour of the use of such words as *proto-* and *per-* rather than of *-ic* and *-ous*. He was rather inclined to agree with Mr. Harcourt's observations in defence of the English. Respecting such words as mono-chloride and bi-chloride of mercury, it is quite true that, if we use them, we mean that the one contains double the quantity of chlorine in the molecule to the other, and not merely double the ratio of the mercury and the chlorine.

The President hoped it would not be understood that he insisted on Latin names in preference to the English. When Latin names are more easily modified than English, by all means use them; but, when such is not the case, refuse them.

It would not be worth while to employ English words instead of the Latin aluminium, chromium, &c.; and it should not be argued that, because we use English words in some cases, that therefore we must use them in all cases. The whole genius of the English language is at variance with such a proposition. We want an intelligible principle to guide us, instead of the fixed names, which imply particular theories of the constitution of bodies. With regard to *-ic* and *-ous* adapting themselves only to one term of a series, he conceived that, as long as we have to do with the properties of bodies in chemistry, the difference between acid and basic bodies will be one of the chief things to refer to; and, if the business of names is to recall the chief properties of bodies, he thought it must be an advantage, in describing terms of a series, to use some name to distinguish those which are not acid from those which are.

Professor Voelcker said that, in one aspect, uniformity of nomenclature has great advantages; but he was not sure that one and the same chemical compound, having two, three, or four different names, was an unmitigated evil. In teaching chemistry, he would not object to a substance being called by the empirical name, if, by this means, certain properties were fixed upon the mind of the student, by which he became familiar with a certain definite substance. He might afterwards be told to call it by another name, and then by a third; and, when he was once familiar with the real nature of the substance, it was immaterial whether he knew it by one name or the other. By the same combination having different names, the teacher would be able to illustrate the different views entertained by chemists of the constitution of a substance.

[P.S. I think we should be justified in considering such names as aluminium, &c., to be naturalised English words: if, indeed, they ever were Latin at all. But this is beside the point; exception is taken, not to the use of a Latin name *quâ* Latin, but to the use of a Latin name where there exists a respectable English name for the same substance.

That system of nomenclature seems to me preferable in which there is the *minimum* of modification (which might prove a disguise) of the names themselves: the necessary variation being gained by prefixes. Take as an instance the nomenclature of the metric weights and measures.—H. G. M.]

VII.—*Contributions from the Laboratory of Owen's College, Manchester.*

1. "On Nontronite," by T. E. Thorpe, Ph.D.*

There exists some doubt among mineralogists as to whether nontronite is to be regarded as a distinct mineral species. Owing to the difficulty of obtaining it in a fit state for investigation, the few analyses hitherto published by Berthier, Dufrénoy, Jacquelin and others have taught us but little concerning its real nature. The following analysis made on a comparatively pure specimen may throw additional light on the constitution of this compound. The sample analysed was discovered unclassified in the mineralogical cabinet at Heidelberg, and was stated by Professor Blum, who was disposed to regard it as pinguite, to have been found in the neighbourhood of Heppenheim in the Bergstrasse.

1·4155 grm. of the substance was heated with fuming hydrochloric acid until the mineral appeared to be completely decomposed; the solution was evaporated to complete dryness, and the separation of the silica effected in the usual manner.

Silica obtained, 0·5680 grm.

The weighed silica was then dissolved in caustic potash and proved to be entirely free from sand or quartz.

To the filtrate from the silica were added a few drops of nitric acid, the solution was boiled and the iron precipitated by ammonia.

Ferric oxide 0·5757 grm.

The weighed precipitate was next dissolved in strong hydrochloric acid, water added, and the solution filtered from a minute quantity of silica which had escaped separation by the previous evaporation.

Silica (not completely separated), 0·0030 grm.

* From the Proceedings Lit. and Phil. Society of Manchester, vol. ix, No. 1, Session 1869–70.

Caustic soda was then added in slight excess to the filtrate, and the ferric oxide again precipitated, washed, ignited, and weighed. The re-precipitated ferric oxide weighed 0·5740 grm. Hence the substance was free from any appreciable quantity of alumina.

To the ammoniacal filtrate a few drops of ammonium oxalate were added, and the precipitate was ignited and determined as caustic lime.

Lime, 0·0380 grm.

On adding sodium phosphate to the filtrate a mere trace of magnesia, appearing only after the lapse of some hours, was found.

The remaining constituent, namely water, was determined by igniting the mineral in a stream of dry carbonic acid carefully freed from air, until the loss of weight appeared constant.

1·1205 grm. substance lost 0·2311 grm. water.

Calculated from the foregoing analysis, the composition of the mineral is as follows:—

Lime	2·68
Magnesia	Traces
Ferric oxide	36·44
Silica	40·30
Water	20·98
	100·40

On subtracting the lime, which evidently may be regarded as an unessential constituent, the percentage composition agrees very well with that required by the formula—

$$Fe_2O_3 3SiO_2 + 5H_2O.$$

	Found.		Calculated.
Ferric oxide	37·24		37·20
Silica	41·29		41·86
Water	21·47		20·94
	100·00		100·00

Nontronite is evidently a product of the decomposition by

weathering of some siliceous mineral rich in iron. It possesses a light green colour, which on the expulsion of water changes to a dark chestnut brown. It is perfectly opaque, and shows no evidence of crystallisation. Its fracture is uneven, and the lustre of its streak resinous. It is unctuous to the touch, yields easily to the nail, and is somewhat harder than talc.

The following analysis by Biewend, made upon a specimen found at Andreasberg, agrees remarkably well with the foregoing determinations:—

Ferric oxide	37·30
Silica.....	41·10
Water	21·56
	99·96

2. "On a New Chromium Oxychloride," by T. E. Thorpe, Ph.D.*

When chromyl dichloride $CrO_2\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$, prepared by heating a mixture of potassium dichromate, sodium chloride, and sulphuric acid, is maintained at a temperature of 180°—190° in a sealed tube for three or four hours, it is almost completely converted into a black solid substance, and on opening the tube when cold a considerable quantity of free chlorine escapes. By exhausting the tubes containing the liquid chloride before subjecting them to heat, I have ascertained that chlorine is the only gaseous product of this decomposition. The black compound invariably contains more or less of the liquid chloride which has escaped decomposition: the greater part of this is easily expelled on gently heating the mass after opening the tube. In order to free it completely from the latter body, the black substance was transferred to a clean tube and heated to 120° (*i.e.* about 2° above the boiling point of chromyl dichloride) in a current of dry carbonic acid gas until its weight appeared constant. The following determination of the amount of chlorine contained in the volatile portion shows that it is simply chromyl dichloride which has remained undecomposed.

* From the Proceedings Lit. and Phil. Society of Manchester, vol. ix, No. 3, Session 1869–70.

0·8741 gram liquid chloride gave 1·6458 grams silver chloride.

Calculated for CrO_2Cl_2.	Found.
45·7 per cent.	46·5 per cent.

The solid substance dried in the manner above described appears as a black unerystalline powder, which when exposed to the air rapidly deliquesces to a dark reddish brown syrupy liquid smelling of free chlorine. When thrown into water it quickly dissolves, forming a dark brown solution, which on standing also evolves chlorine. In the nitric acid solution hypochlorous acid appears to be produced. In strong hydrochloric acid the substance dissolves with a dark brown colouration; and on boiling the solution, chlorine is evolved, the liquid becomes greenish yellow, and ultimately changes to the dark green colour peculiar to a solution of chromium sesquioxide in hydrochloric acid. When it is thrown into dilute ammonia, chromic acid is dissolved, together with all the chlorine, and a precipitate is formed possessing the properties of the chromate of chrome sesquioxide ($Cr_2O_3CrO_3$) described by Storer and Eliot. Upon this decomposition is based the method which I have employed for the estimation of the amount of chlorine contained in this body. The weighed quantity of the substance was treated with very dilute ammonia; the solution boiled for a few minutes and filtered; the precipitate well washed by hot water; an excess of nitric acid added to the filtrate; and the chlorine precipitated by the addition of silver nitrate. Two determinations of chlorine carried out in this manner on preparations made at different times gave the following results:—

Preparation I.

0·5900 gram substance gave 0·4870 gram silver chloride and 0·0069 gram metallic silver.

Preparation II.

0·493 gram substance gave 0·4250 gram silver chloride.

Prep. I	20·80 per cent. Cl.
Prep. II	21·32 ,,
Mean	21·06.

In order to determine the amount of chromium it contains, a weighed portion of the substance was repeatedly heated with

strong hydrochloric acid on a water-bath until the evolution of chlorine entirely ceased: the solution was then diluted with water, heated to boiling, ammonia added in slight excess, and the solution again boiled until the supernatant liquid appeared perfectly colourless. The precipitated chrome sesquioxide was then filtered, dried, and weighed.

Preparation I.

0·3442 grm. substance gave 0·2470 grm. chrome sesquioxide.
0·5900 „ „ „ 0·4235 „ „ „

Preparation II.

0·5082 grm. substance gave 0·3590 grm. chrome sesquioxide.
0·5942 „ „ „ 0·4210 „ „ „

Prep. I	49·30	per cent. Cr.
	49·25	„
Prep. II.	48·45	„
	48·62	„
Mean	48·91	„

Hence the percentage composition of the substance is as follows:—

	Found.	Ratios.	Calculated.
Chlorine.....	21·06	2	21·86
Chromium....	48·91	3	48·54
Oxygen.....	30·03	6	29·60
	100·00		100·00

I have attempted to control the above empirical formula ($Cr_3O_6Cl_2$) by heating a weighed portion of the substance in hydrogen. The action of hydrogen upon the new chloride when heated is extremely energetic. At a comparatively low temperature it takes fire, combustion proceeds rapidly throughout the mass, and ultimately the substance is converted into chrome sesquioxide, hydrochloric acid, and water. Care must be taken to regulate the current of hydrogen, since, if it is too rapid, particles of the finely-divided sesquioxide are apt to be mechanically carried away. From an experiment in which the gas was carefully purified from oxygen by passing it through strongly alkaline pyrogallate solution and over heated metallic copper, and then dried by transmitting it through

tubes containing pumice moistened with strong sulphuric acid, the following numbers were obtained:—

0·8715 grm. substance gave 0·6150 grm. chrome sesquioxide.
Found 70·58 per cent. Cr_2O_3.
$Cr_3O_6Cl_2$ gives by calculation 70·72 „

I had an additional object in thus studying the action of hydrogen upon the new chloride. I considered that this action might possibly throw some light on the constitution of this compound. The new oxychloride may, in conformity with the analytical results, be regarded as a compound of chromous chloride with two equivalents of chromium trioxide. Now, chromous chloride, according to Moberg, may be heated in hydrogen to the softening point of glass without suffering decomposition; and if it were found that water was the only volatile product of the reaction, we should possess a certain amount of evidence for supposing that the formula $CrCl_2 . 2CrO_3$ represents the constitution of this substance. Experiment showed, however, that the chlorine was not so firmly united in this compound as in the chromous chloride: on gently heating the substance in hydrogen, hydrochloric acid was immediately evolved.

Péligot has described a series of salts to which are assigned the general formulæ $M Cl . CrO_3$ and $M''Cl_2 . 2CrO_3$, where M represents a univalent metal and M″ a bivalent metal. The following are the names and formulæ of the salts prepared by Péligot:—

$K Cl . CrO_3$	Potassium chlorochromate.
$Na Cl . CrO_3$	Sodium chlorochromate.
$NH_4Cl . CrO_3$....	Ammonium chlorochromate.
$Mg Cl_2 . 2CrO_3$..	Magnesium chlorochromate.
$Ca Cl_2 . 2CrO_3$..	Calcium chlorochromate.

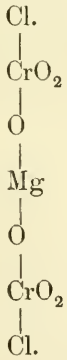
Now the new oxychloride stands in a very evident relation to these compounds. Supposing for a moment that the formulæ given to these substances correctly represent their constitution, then the new oxychloride may be regarded as the chromium term of the series—bivalent chromium replacing magnesium or calcium.

$$Cr''Cl_2 . 2CrO_3,$$

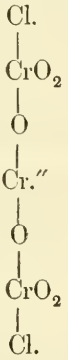
a formula identical with that of which I have just attempted

to show the impropriety. But there is still another reason for supposing that a compound thus constituted could not exist. Chromous chloride is one of the most energetic deoxidising agents known, and we can hardly conceive it to be united in a stable compound with a substance which so readily parts with its oxygen as chromium trioxide. Hence I am disposed to regard the constitution of the salts of Péligot as very different from that implied by the above method of representation: indeed, to the best of my knowledge, the general formula assigned to these salts expresses not a single experimental fact, unless it be the mode of their decomposition by water; probably it had reference to the views of Rose and Berzelius respecting the constitution of the so-called chlorochromic acid. The following structural formulæ better represent in my opinion the constitution of these compounds and their relation to chromyl dichloride.

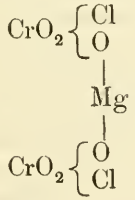
Magnesium Chlorochromate.

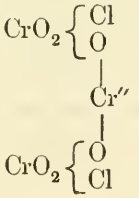


Chromium Chlorochromate.



These substances may also be thus represented:—





The relation of the new oxychloride to chromyl dichloride is thus very apparent. Three molecules of chromyl dichloride when heated are resolved into one molecule of chromium chlorochromate and four atoms of chlorine.

VIII.—*Observations on the Solution of Gases in Water.*

December 16th, 1869.

Dr. Williamson, President, in the Chair.

THERE being no formal papers before the Society on this occasion, the President requested Mr. McLeod to communicate the result of his observations on the Gases in Sea-water.

Mr. McLeod, alluding to the opinion which appears to be entertained by some persons that sea-water taken from great depths effervesces when brought to the surface, expressed his belief that this idea is quite erroneous. Mr. Hunter, in his recent experiments on sea-water taken from great depths, found only 2·8 volumes of gas in 100 volumes of the water, a quantity much less than that contained in ordinary Thames water, which, as every body knows, does not effervesce when drawn from a tap. He (Mr. McLeod) had lately made some experiments on the quantity of gas contained in Thames water, which had been kept in a cistern and drawn from a tap; 100 volumes of this water were found to contain—

	Volumes.
Nitrogen	1·398
Oxygen.....	0·619
Carbonic anhydride.....	4·180
Total.....	6·197

As, however, the quantity of gas dissolved in sea-water may be affected by the presence of the saline constituents, he had also experimented on a sample of sea-water collected near Worthing, which had been exposed to the air for 21 months—at least kept in a half-filled bottle—and had probably, therefore, taken up as much oxygen and nitrogen as it was capable of holding. 100 volumes of this sea-water were found to contain—

	Volumes.
Nitrogen	1·104
Oxygen.....	0·572
Carbonic anhydride.....	2·620
Total.....	4·296

This is a much larger quantity than that found by Mr. Hunter, viz., 2·8 volumes in 100, whence it may be inferred that sea-water taken from great depths is very far from being saturated with gases, and cannot, therefore, exhibit any tendency to give off gas when brought to the surface.*

The President remarked on the importance of attending to the effect of soluble matter in water, or its power of holding gases in solution. He then called on Dr. Hugo Müller to communicate his observations on the condition of carbonic acid gas when dissolved in water.

Dr. Hugo Müller said that, in making some experiments in connection with the manufacture of soda-water, he had found that, in order to make the water take up carbonic acid gas in such a manner that the gas may not be immediately disengaged when the liquid is let out of the apparatus, it is necessary that the gas and water be left together in the apparatus for at least 24 hours. If the agitation is continued merely for an hour or an hour and a-half, then, on letting out the water, the carbonic anhydride instantly disengages itself, the water becomes creamy, the gas comes up immediately, and the effervescence

* Since the above remarks were made, Mr. Hunter's paper has been printed, and on carefully examining his numbers (which was scarcely possible when the communication was read), it will be seen that the comparatively small quantity of gas which he obtained from the sea water was accounted for by the fact that a much smaller amount of carbonic anhydride was obtained by him than from the water collected at Worthing, though the quantities of nitrogen and oxygen were considerably larger. The largest proportions of nitrogen and oxygen were obtained by Mr. Hunter from water collected on July 27th, from a depth of 450 fathoms, the temperature of the water at that depth being 47°·6 F. (8°·7 C.). This contained in 100 volumes 1·457 vols. of nitrogen and 0·021 of oxygen (the same quantity of oxygen but less nitrogen was also obtained from a depth of 500 fathoms on July 23rd), and would therefore begin to evolve gas at a temperature of 14°·6 C., that is, if nitrogen is soluble in sea-water to the same extent as in distilled water. This quite accords with Mr. Hunter's statement, that the water contained so much gas that it began to evolve it on a slight elevation of temperature.

In the case of the water from Worthing, no precaution was taken to saturate it with air, it being merely left, as stated, in a partially filled bottle. If it had actually absorbed as much nitrogen as it was capable of retaining, it would appear that this gas is more soluble in distilled than in sea-water.—H. M.

Mr. Hunter, in a letter to the Editor, relating to this matter, says that he is not aware of any official statement having been made that sea-water brought up from great depths effervesced like soda-water. Mr. W. L. Carpenter, who accompanied the expedition on the first cruise, told him that he could not understand how the mistake arose, as he had never observed any such phenomenon. The waters examined by Mr. Hunter on board H.M.S. "Porcupine," did not, of course, exhibit any tendency to give off gas till they were heated.

is over; whereas, if the gas be allowed to remain in contact with the water from 20 to 24 hours, and the liquid be then let out, the carbonic anhydride disengages itself from the water gradually, and attaches itself to the sides of the glass, seeming, indeed, to be altogether in a different state to that in which it is, after being left for only a short time in contact with the water. It appears, indeed, that in the one case, that is, after a short contact, the carbonic anhydride dissolves in the water merely as such, but that after prolonged contact it becomes hydrated, and is dissolved by the water as hydrogen carbonate, or carbonic acid, and is then retained more firmly.

Dr. Müller mentioned also another observation which he had made in connection with this subject, namely, that on putting a very small quantity of common salt into the apparatus, together with the water which is to be carbonated, the whole process of dissolution takes place much more quickly, the acceleration being probably due to decomposition of the sodium chloride by carbonic acid, hydrochloric acid being formed together with bi-carbonate of soda. He could not say positively whether the whole of the chlorine present is thus set free as hydrochloric acid, but he had ascertained the presence of that acid by means of ultramarine, which is known not to be acted upon by carbonic acid or by sodium chloride, but is acted upon by the carbonated water made in the way just described. The liberation of an acid in this reaction may therefore be inferred. In connection with this subject, it may also be mentioned that on passing carbonic acid gas through a neutral or even slightly acid solution of chloride of lead, a turbidity is produced after a short time, but not immediately. In a certain time, indeed, a precipitate is formed, consisting of the double salt of carbonate and chloride of lead. This compound is also found in nature, and, indeed, the reaction just noticed, seems to explain the circumstance that in nature we never find pure chloride of lead, except as a sublimate in volcanoes. In all other cases the chloride of lead is found associated with carbonate, forming the mineral called "chloro-carbonate of lead," and there is no doubt that this salt, being formed in nature by an aqueous process, the ever present carbonic acid has partly decomposed the chloride of lead, and formed this chloro-carbonate. This is another instance in which a chloride is decomposed by carbonic acid, and there can be no doubt that this decomposition is of frequent occurrence.

Dr. Divers observed that on mixing rectified spirit with ordinary distilled water, which contains air from having undergone exposure, there is a kind of effervescence, the liquid becoming milky, just as if a precipitate were forming. This effect is due to the liberation of extremely minute bubbles of air, and seems to show that the mixture of spirit and water has less solvent power for air than for water itself.

The President said that it would be interesting to know whether the temperature has any connection with the peculiar state observed by Dr. Müller in the dissolved carbonic acid, more especially as the recent experiments of Dr. Andrews on the liquefaction of carbonic acid at different temperatures have shown that a few degrees of temperature make a very great difference in the properties of the carbonic acid—a difference of property not to be overcome by multiplying the pressure enormously.

Dr. Müller's observations on the greater solubility of carbonic acid in water containing sodic chloride, appeared to him (the President) to be of considerable theoretical value, more especially when confirmed as they were by his observation upon ultramarine, when used as a test for free hydrochloric acid. In connection with this subject he drew attention to the conclusion at which he had himself arrived some time ago respecting the state in which salts, such as sodic chloride, dissolve in water, namely, that they generally dissolve by decomposition; in fact that when two liquid substances are in presence of one another, as binary compounds, they are present not only as such, but at each moment also, to some extent, as the products resulting from the interchange of their particles; so that sodic chloride for example, when dissolved in water, does, to some extent, consist of the products formed by the interchange of sodium and hydrogen, that is to say, of hydric chloride and sodic hydrate. The proportion between the two original compounds and the substances formed by their decomposition, depends upon the relative velocities of the movements which decompose the original compounds, and of the movements which reproduce them.

These things, from their very nature, are extremely difficult to prove; they are processes of rapid motion or interchange, and the substances in question cannot be fixed in any particular state, except by removing them from the sphere of decomposi-

tion. If by any such interchange an insoluble compound would be formed, we know that it is actually formed, because if a small quantity of silver chloride, for example, is produced, it immediately goes down and is removed from the circle of decomposition, so that the reproducing change between it and the correlative compound takes place much more slowly, perhaps indeed at a rate incomparably slower, than that with which the decomposing change has taken place. Dr. Müller's case is one which bears in a very direct and important manner on the general proposition, and his introduction of ultramarine as a test for the discovery of free hydrochloric acid seems to afford a strong confirmation of the views above detailed. The ultramarine is decomposed by hydric chloride, but not by sodic chloride, and therefore its decomposition in the case above alluded to seems to furnish very good evidence that hydric chloride is present in the liquid. It is hardly likely that so weak an acid-salt as hydric carbonate could expel hydric chloride, except in infinitesimally small quantities, but if soda is present in any way in the liquid, the carbonic acid added to it will combine with it, and diminish the rapidity with which the reverse changes take place. The other reaction of the carbonic acid and chloride of lead is also an exceedingly interesting observation on the same kind of reaction.

Dr. Hugo Müller observed that in the last mentioned experiment it is much easier, than in the former case, to ascertain whether the action has really taken place, because the solution can be warmed, and some of the liberated acid distilled over; besides the reaction is completed more quickly. It might be imagined that by heating the mixture of chloro-carbonate and carbonic water, the *status quo* would be gradually reproduced; but this is not the case; a certain amount of the original compounds is indeed reproduced; nevertheless, a certain quantity of hydrochloric acid can be actually distilled over, and, of course a proportional quantity of lead carbonate will remain as ultimate residue.

The President, in further illustration of the principles above considered, referred to some experiments which he made about twenty-five years ago, on the action of chlorine on water in presence of salts like sodic sulphate. Chlorine in contact with water forms hydrochloric and hypochlorous acids: $Cl_2 + HHO = HCl + HClO$, as is shown by the fact that on adding silver

nitrate to the solution, half the chlorine is precipitated as silver chlorides, while the liquid retains its bleaching power undiminished. Moreover, aqueous chlorine decomposes sodic sulphate and other neutral salts, even calcic carbonate and other similar compounds. He remembered making a considerable quantity of hypochlorous acid by leaving aqueous chlorine in contact with sodic sulphate, the reaction most probably consisting in this, that the sodic sulphate in presence of water was partly converted into hydric sulphate and sodic hydrate, which latter reacted with the chlorine so as to form sodic chloride and hypochlorous acid. There is no doubt that these actions of masses are not sufficiently attended to.

IX.—*Contributions to the History of Explosive Agents.*

By F. A. Abel, F.R.S., Treas. Chem. Soc.

(Abstracted by the author from the Philosophical Transactions for 1869.)

The degree of rapidity with which an explosive substance undergoes metamorphosis, as also the nature and results of that metamorphosis, are, in the greater number of instances, susceptible of several modifications by variations of the circumstances under which the conditions essential to chemical change are fulfilled. Gun-cotton furnishes an excellent illustration of the manner in which such modifications may be brought about. If a loose tuft or large mass of gun-cotton wool be inflamed in open air by contact with, or proximity to, some source of heat, the temperature of which is about 135° C. or upwards, it flashes into flame with a rapidity which appears almost instantaneous, the change being attended by a dull explosion, and resulting in the formation of vapours and gaseous products, of which nitrogen-oxides form important constituents. If the gun-cotton be in the form of yarn, thread, woven fabric or paper, the rapidity of its inflammation in open air is reduced in proportion to the compactness of structure or arrangement of the twisted, woven, or pulped material; and if it be converted by pressure into compact masses, solid throughout, the rate of its combus-

tion will be still further reduced. If to a limited surface of gun-cotton, when in the form of a fine thread or of a compactly pressed mass, a source of heat is applied, the temperature of which is sufficiently high to establish the metamorphosis of the substance, but not adequate to inflame the products of that change (carbonic oxide, hydrogen, &c.), the rate of burning is so greatly reduced that the gun-cotton may be said to smoulder without flame, as shown by me in a communication to the Royal Society in 1864*; the reason being that the products of change, which consist of gases and vapours, continue, as they escape into air, to abstract the heat developed by the burning gun-cotton so rapidly that it cannot accumulate to an extent sufficient to develope the usual combustion, with flame, of the material.

For similar reasons, if gun-cotton be kindled in a rarefied atmosphere, the change developed will be slow and imperfect in proportion to the degree of rarefaction, so that, even if an incandescent wire be applied, in a highly rarefied atmosphere, to the gun-cotton, it can only be made to undergo the smouldering combustion until the pressure is sufficiently increased by the accumulating gases to reduce very greatly the rate of abstraction, by these, of the heat necessary for the rapid combustion or explosion of the substance.†

If, on the contrary, the escape of the gases from burning gun-cotton be retarded, as by enclosing it in an envelope or bag of paper, or in a vessel of which the opening is loosely closed, the escape of heat is impeded until the gases developed can exert sufficient pressure to pass away freely by bursting open the envelope or aperture, and the result of the more or less brief confinement of the gases is a more rapid or violent explosion, and consequently more perfect metamorphosis of the gun-cotton. So, within obvious limits, the explosion of gun-cotton by the application of flame or any highly heated body is more perfect in proportion to the amount of resistance offered in the first instance to the escape of the gases; in other words, in proportion as the strength of the receptacle enclosing the gun-cotton, and the consequent initial pressure developed by the explosion, is increased. Hence, while gun-cotton has been found too rapid or violent in its explosive action when confined in guns, and has proved a most formidable agent of destruction

* Proceedings of the Royal Society, vol. xiii, p. 213. † Ibid., p. 205.

if enclosed in metal shells or other strong receptacles, it has hitherto been found comparatively harmless as an explosive agent if inflamed in open air or only confined in weak receptacles.

Other explosive compounds, and also explosive mixtures, are similarly influenced, though generally not in such various ways, by the circumstances attending their metamorphosis. Thus the rapidity of the explosion of gunpowder is modified by variations in its density and state of division, and in the degree of facility afforded for the escape of the generated gases, and consequently of the heat which is disengaged during the explosion. Mercuric fulminate may be inflamed in open air upon a piece of very thin sheet metal without indenting it, and furnishes under these circumstances a comparatively feeble explosion; but if even a very much smaller quantity be enclosed in a case or receptacle made of the same description of sheet metal, the latter will be shattered into many pieces when the fulminate is inflamed, and the explosion will be attended by a violent report.

Modifications, apparently slight, of the manner in which the source of heat is *applied* to these explosive agents, when exposed to air under circumstances in other respects uniform, suffice to modify the character of their explosions in a remarkable manner. Thus a modification of the position in which the source of heat is placed with reference to the body of a charge of gunpowder, which is only partially confined, suffices to alter altogether the character of the explosion produced. This is illustrated by the following experiment.

A cylindrical case of sheet tin, 2·5 inches diameter, 6 inches long, and open at one end to its full diameter, was inserted up to its opening in stiff clay soil, which was tightly rammed round it. The cylinder was filled with fine-grain gunpowder (about 1 lb.), and the charge was inflamed by means of a small electric fuse inserted just beneath the exposed surface of powder. The latter burned with a violent rushing sound, similar to, only of much less duration than that produced by the first ignition of a rocket, and indicating a rapidly successive ignition of layers of the powder. The canister was split open in the soldered seam, but was not thrown out of the hole. A small quantity of earth was thrown up, but fell back into the hole. A second corresponding charge of gunpowder was arranged in precisely the same manner as in the preceding experiment, and was in-

flamed by means of an electric fuse placed at the *bottom* of the charge. A loud explosion was produced; much earth was thrown up and scattered, the bottom of the tin case was found in the crater produced, but the body of the case was not recovered; it had evidently been projected to a considerable distance. In this experiment the main body of the charge obviously acts, at the moment of ignition, as tamping does in a blast-hole, by presenting a resistance to the escape of the gases generated, and thus for a moment establishing the pressure essential to the violent or perfect explosion of the portion of gunpowder first inflamed, whereupon the same character of explosion extends throughout the charge.

Mercuric fulminate furnishes still more striking illustrations of the manner in which the position of the source of heat, with reference to the main body of the explosive material to be inflamed, influences the character of the explosion. In firing some charges of mercuric fulminate, freely exposed, by means of small electric fuses, it was observed, on the one hand, that a small quantity (0·65 grm. = 10 grains) produced occasionally a very much more violent explosion than was obtained with double the quantity of the same fulminate inflamed apparently in the same way, and, on the other hand, that equal quantities of the fulminate, successively inflamed, produced, in one instance, a dull report, such as is well known to be furnished when flame is applied to a small quantity of freely exposed fulminate, while in the other instance a very sharp detonation was obtained, like that observed when a small quantity of closely confined fulminate is exploded. Believing that this remarkable difference of result might perhaps be caused by a variation in the force of explosion of the small electric fuse, I substituted a platinum-wire for the latter as the inflaming agent, and still the same variable results were obtained. These were at first thought to be due to a variation in the surface of the fulminate heated at one time, but they were soon traced to variations in the *position* of the source of heat. 1·32 grm. (25 grains) and 2·64 grms. (50 grains) of the fulminate, inflamed by allowing the incandescent wire just to touch the top or edge of the heap, exploded with a dull report, and produced no effect upon the thin flat plate of copper sheet upon which they rested; but about 1 grm. (15·5 grains) of the same fulminate, heaped up over the platinum-wire, produced a sharp and

violent explosion, the force of which deeply indented and bent up the support of sheet copper. Equal quantities of the fulminate were made to explode feebly or detonate violently at pleasure, simply by varying their arrangement with reference to the position of the source of heat.

A few substances, of which the metamorphosis into gaseous products and vapours is developed by much less powerful impulses from without than those just instanced, the explosion of which is therefore determined by but little elevation of temperature or by the application of slight disturbing impulses of a mechanical or chemical nature, would appear at first sight only to a small extent susceptible of modifying influences similar to the above. The direct application of but little heat, or the production of a slight increase of temperature by gentle friction or pressure, or by the development of chemical action in some very small portions of the mass, suffices to explode the chloride or iodide of nitrogen, or silver-fulminate; and the explosion of one particle developes an impulse so greatly in excess of that required to disturb the chemical equilibrium existing among the molecules of the mass, that instantaneous decomposition ensues throughout. The great proneness to change of these substances when exposed to a slight disturbing influence, is illustrated by the fact that a concussion imparted to the air in a spacious apartment in which the iodide of nitrogen has been placed, by means of a small explosion or detonation, or even by the violent slamming of a door, suffices to bring about the explosion of that substance. But even if *these* bodies be so confined that an initial resistance is offered to the escape of the gaseous products of their explosion, the violence of the detonation is greatly increased, the development of explosive force being restricted to the instant of rupture of the envelope by the compressed gases. Thus the violence of explosive force exerted by a small quantity of silver-fulminate, confined in a case of stout sheet metal, is very decidedly greater than if a corresponding quantity be enclosed in metal foil, or freely exposed to air and inflamed in the same manner. The violence of explosion of iodide of nitrogen has been found to be very decidedly increased by enclosing it in an envelope or shell of plaster of Paris, or, better still, in a case of sheet metal, while the chloride of nitrogen explodes with but comparatively little

violence, unless it is confined. The reputation which this substance has enjoyed of being the most violent explosive body known, appears to have been due to the fact that experiments on its explosion have always been conducted with a covering of water upon the material. Three or four drops (about 0·14 grm. = 2 grains) placed in a watch-glass covered only with a thin layer of water, explode with a sharp report when touched with turpentine, and almost pulverize the glass; but similar quantities, of which the upper surfaces were exposed to air, have been repeatedly exploded in watch-glasses without breaking the latter. 2 grms. of the chloride, contained in a watch-glass, and covered with a thin layer of water, were placed upon a small solid cylinder of hard *papier maché* which rested upon paving. A violent explosion was produced by touching the chloride with turpentine, the watch-glass was pulverized and dispersed, and the cylinder was greatly shattered, fragments being projected in all directions. 4 grms. of the chloride, with the upper surface exposed to air and placed upon a similar cylinder of *papier maché*, produced a comparatively very feeble explosion; the watch-glass was broken, but the cylinder was not in the slightest degree affected, and remained undisturbed in its original position. A repetition of the experiment with 4 grms. of the chloride, enclosed by a thin layer of water, produced complete disintegration of the cylinder. It appears from these results that in the case of the chloride of nitrogen, the decomposition of which is of an instantaneous character, the resistance offered at the moment by the layer of water acts as effectually in intensifying the force of explosion, as a thin sheet metal case does with the mercuric fulminate, or as a strong iron shell with gun-cotton or gunpowder.

The product of the action of nitric acid upon glycerin, which is known as nitroglycerin or glonoin, and, as regards its power of sudden explosion, bears some resemblance to the chloride and iodide of nitrogen, appears to be susceptible of only two varieties of decomposition. If a sufficient source of heat be applied to some portion of a mass of this liquid in open air, it will inflame and burn gradually without any explosive effect; and even when nitroglycerin is confined, the development of its explosive force by the simple application of flame or of other sources of heat, by the ordinary modes of operation, is difficult and

very uncertain. But if the substance be submitted to a sudden concussion, such as is produced by a smart though not very violent blow from a hammer upon some rigid surface on which the nitroglycerin rests, the latter explodes with a sharp detonation, just as is the case with gun-cotton. Only that portion of the explosive agent detonates which is immediately between the two surfaces brought into sudden collision; the confinement of this portion between the hammer and the support, combined with the instantaneous decomposition of the portion struck, prevent any surrounding freely exposed portions from being similarly exploded by the detonation. A similar result is obtained if *any* explosive compound or mixture be submitted to a sufficiently sharp and violent blow, but the tendency of surrounding particles to become inflamed by the detonation is in direct proportion to the rapidity of explosive action of the substances.

The practical difficulties and uncertainty which attend attempts to develope the explosive force of nitroglycerin by the agency of flame or the simple application of any highly heated body, even when the material is confined in strong receptacles (such as iron shells or firmly tamped blast-holes), appeared fatal to any useful application of the powerful explosive properties of this substance, until M. Alfred Nobel's persevering labours to utilize nitroglycerin, eventually resulted in the discovery of a method by which the explosive power of the liquid could be developed with tolerable certainty. M. Nobel first employed gunpowder as a vehicle for the application of nitroglycerin. By impregnating the grains of gunpowder with that liquid, he added considerably to the destructive force of the powder when exploded in the usual way, in closed receptacles. M. Nobel's subsequent endeavours to apply nitroglycerin *per se* were based upon the belief that its explosion might be effected by raising some portion of a quantity of the liquid to the temperature necessary for its violent decomposition, whereupon an initiative explosion would be produced which would determine the explosion of any quantity of the substance.

I have never succeeded in effecting the *explosion* of nitroglycerin by simply bringing it into contact with an inflamed or incandescent body, but the following results illustrate the manner in which a score of heat may operate in accomplishing the explosion of this substance.

A piece of very thin platinum wire, stretched across between the terminals of two insulated copper wires, was immersed in nitroglycerin; these wires were connected with a Bunsen battery of five large cells, and a second piece of platinum-wire, similar to that immersed in the liquid, was introduced into the circuit. This was then completed, with the intervention of a long piece of platinum-wire between one of the conducting-wires and the battery. The resistance presented by this interposed platinum-wire was gradually reduced by shortening it, until ultimately the short platinum-wire not immersed in the nitroglycerin was fused. The latter was not exploded nor inflamed, nor was the wire enclosed in it fused, the heat developed in the latter being rapidly absorbed by the surrounding liquid and removed by convection. A very much thicker platinum-wire was now substituted for the thin one, and immersed in the liquid; a second short piece was not interposed in the circuit in this instance, but a long platinum-wire, of the same thickness as the above, was employed, as a means of gradually reducing the resistance in circuit. When the length of this wire had been reduced to five inches, it was raised to bright redness; this state of things was maintained for about one minute, but the short wire in the nitroglycerin did not glow at the expiration of that period, nor did the liquid exhibit any signs of change, but the glass vessel containing it had become very warm. The long platinum-wire was then removed, and the full battery-power was passed into the short wire immersed in the liquid. After the lapse of about one minute the latter began to assume a brownish colour (like that of a solution of iron), which rapidly deepened, though no red vapours were perceptible in the upper portion of the vessel, until after the lapse of 90 seconds, when the nitroglycerin exploded with great violence. Several unsuccessful attempts were afterwards made to explode nitroglycerin by means of the electric spark, but eventually, by allowing the sparks from a Ruhmkorff coil with a Leyden jar attached to pass uninterruptedly between the poles, which were just touching the liquid, the latter being splashed up by the discharges, the surface of the liquid speedily darkened, and in 30 seconds it exploded.

It is evident from these results that nitroglycerin can be *exploded* by electric agency, or by direct application of any other source of heat only, if the intensity of the latter, or the period

during which it is applied, suffices to develope decomposition in some portion of the liquid; when once this is established, the temperature is soon raised by accumulation of heat (especially if the application of external heat be continued) until it attains the point at which explosion occurs.*

* In experiments instituted some time since on the action of heat upon nitroglycerin, I found that a small quantity (one or two drops) of pure nitroglycerin, if exposed to a very gradually increasing temperature, might be raised to 193° C. (380° F.) without the occurrence of an explosion; the liquid sustained slow decomposition until it was entirely deprived of explosive properties. A larger quantity enclosed in a sealed tube, was exposed for four days to a temperature of 100° C. without exploding. At the expiration of that period the liquid had assumed a brownish colour, but this gradually disappeared altogether after the tube had cooled down; and when the latter was opened after the lapse of some days, there was no pressure of gas, nor did the liquid exhibit the slightest acidity. In this instance the decomposition, probably resulting in the liberation of the nitrogen-oxides, was established by the continued exposure to 100°, and would doubtless, as in the case of the electric experiments, have gradually increased if the application of heat had been continued until the internal development of heat had resulted in explosion.

The difference in the behaviour of nitroglycerin and gun-cotton, when exposed to the influence of a source of heat (apart from the difference in the heat required for their explosion), is evidently due principally to the difference in their physical condition. When a heated body is applied to nitroglycerin, the liquid nature of the latter leads to the distribution through its mass of the heat applied, with rapidity sufficient to render the *ignition* of the but slightly volatile liquid a matter of difficulty, even by the application of a very highly heated body, such as a red-hot wire or rod, or a piece of burning wood; and when the liquid is actually inflamed it burns at first non-explosively, because the increase in temperature of the body of liquid (or of that part presented by the burning surface) which is necessary for developing its sudden decomposition or explosion, takes place only gradually. But if by establishment of a slow decomposition throughout or in some portion of the nitroglycerin, a tendency to disruption of the constituent-molecules is developed, the disturbance of chemical equilibrium favours the action of any impulse from without, such as the direct application of heat, so that the *violent explosion* or sudden decomposition of the mass is determined by applying heat to an extent which would, under normal conditions, be quite inadequate to bring about such a result.

In the case of the solid and badly conducting substance, gun-cotton, when a source of heat just sufficient for its ignition is applied to any portion, the heat is not diminished by distribution through the mass, hence the particles of gun-cotton contiguous to the source of heat are inflamed almost immediately. If the gun-cotton be in a loose or porous condition (*e.g.*, in the form of wool or of loosely wound thread), the entire mass will inflame with such rapidity as to produce a species of explosion, on account of the rapid penetration to the surrounding particles of the heat resulting from the first ignition; but if it be in a compact (compressed) mass, in which the contiguity of particles more nearly approaches that of the particles in the liquid nitroglycerin, the gun-cotton proceeds to burn gradually from the exterior towards the centre of the mass.

If gun cotton be exposed to a source of heat *insufficient* for its ignition, the heat will gradually accumulate in those parts most contiguous to the source, spreading

M. Nobel has described various devices for effecting this so-called *initiative* explosion of some portion of a nitroglycerin charge, of which evidently the most successful are the explosion of a small confined charge of gunpowder, or of a large percussion-cap, when immersed in or placed immediately over the nitroglycerin. M. Nobel, however, classes these two modes

with comparative tardiness through the mass. A twofold result will then be obtained; heat eventually accumulates to an extent sufficient to establish chemical change in the mass, which becomes greatest near the source of heat, so that, if the application of the latter be not interrupted, the temperature requisite for ignition will be speedily attained in those portions: the result will, however, be no longer the simple inflaming of the gun-cotton with more or less rapidity, but an explosion will ensue, as in the case of nitroglycerin, the violence being proportionate to the heat which has accumulated, and to the extent to which a disturbance of chemical equilibrium has been established.

Frequent confirmations of this view have been obtained in the course of my investigations on the effects of heat upon gun-cotton. The violence of explosion of samples of gun-cotton confined in flasks with not very narrow necks, which had been for some time previously undergoing decomposition (from long-continued exposure to temperatures considerably below its inflaming-point), was always very much greater than would have been the case had gun-cotton in the flasks been ignited by the momentary application of a highly heated body. It would appear, from temperature-observations carried on during experiments of this kind ("Phil. Trans.," vol. clvii, pp. 197, 223, 226), that in those instances the great violence of explosion was to be ascribed in part to the rapid accumulation of heat in the mass of gun-cotton when the decomposition had reached particular stages; but there can be no question that, at the period immediately preceding the explosion, the gun-cotton was in a state of high chemical tension, and readily susceptible of instantaneous chemical change throughout, just as a Rupert's drop is readily susceptible of violent mechanical disintegration; so that the passage from gradual to instantaneous and therefore most violent decomposition, would occur as soon as the accumulation of heat attained the point at which a sufficient disturbing impulse was imparted to the mass.

The following series of experiments appear confirmatory in their results of the conclusions drawn from the accidental results obtained in the experiments just alluded to.

A wide test-tube was filled to about one-fourth with gun-cotton, the mouth of the tube was left open, and the gun-cotton was inflamed by means of a platinum-wire heated by electricity. A faint explosion was the result, accompanied by a considerable body of flame, and a portion of the gun-cotton was projected from the tube unburned.

The experiment was repeated, the tube being immersed for several minutes in a water-bath, at a temperature of 100° C., so that the gun-cotton was raised throughout to that temperature immediately before it was inflamed. The explosion was decidedly, though not very greatly, more vehement than before; the tube was not shattered.

A broad piece of thin platinum-foil, about 2 inches long, was attached by its two sides to copper wires leading to the poles of a battery, sufficient resistance being introduced into the circuit to prevent the foil from being raised to a higher tempera-

of ignition in which an explosion or detonation is applied as the exploding agency, together with various others in which the simple application of a high temperature to some portions of the nitroglycerin is proposed as the means of explosion; and although, in his published description of these various methods, he refers to difficulties in developing explosion by those which relate to the simple application of flame or other heated body to the nitroglycerin, yet he refers the effect produced by the confined charge or the percussion-cap only to the heat developed by the ignition of these exploding agents.

The circumstance that nitroglycerin, or any preparation of that substance, may be violently exploded *when freely exposed to air*, by the explosion in contact with it of a small confined charge of gunpowder, or of a detonating substance, while other modes of explosion by the application of heat or flame, which have been described by M. Nobel, only develope explosion under special conditions, points to a decided difference between the action of the two modes of ignition, and appears to indicate that it is not simply the heat developed by the chemical change of the gunpowder or detonating powder which determines the explosion of the nitroglycerin.

An experimental investigation of this subject has left no doubt on my mind that the explosion of nitroglycerin through

ture than 90°—100° when the circuit was completed. The wires were approached to each other, so that the strip of foil formed a species of tube open at both ends and down the side. A similar quantity of gun-cotton to that used in the preceding experiments was placed inside this tube, being therefore nearly surrounded by the foil. The whole arrangement was then introduced into a test-tube, like those used in the preceding experiments, and the voltaic circuit was completed. In the course of a few minutes the odour of decomposing gun-cotton was perceptible at the opening of the tube; faint nitrous vapours were soon afterwards observed, and within about fifteen minutes after the first application of heat, the gun-cotton exploded very sharply with only a faint flash, and the tube was shattered and violently dispersed.

The great violence of the explosion at Woolwich, in 1865, of about 140 lbs. of gun-cotton which had been exposed to elevated temperatures for ten months, and of which some packages, very imperfectly purified, were known to be in a state of decomposition at the time ("Phil. Trans.," vol. clvi, p. 243, *et seq.*), can scarcely be ascribed only to the circumstances that the gun-cotton had been closely packed in strong cases, and that the packages of gun-cotton were at a temperature of about 50° C. at the time of the explosion. When the decomposition, established in some small portion of the gun-cotton, had attained the condition resulting in explosion, a large quantity of the material was in a state of incipient change, and, therefore, in a favourable condition for sudden metamorphosis; and this circumstance must have greatly contributed to the suddenness and consequent violence of the explosion.

the agency of a small detonation is due, at any rate in part, to the mechanical effect of that detonation, and that this effect may operate in exploding the nitroglycerin quite independently of any direct action of the heat disengaged by the gunpowder or other detonating charge.

I was led to examine into this question by an interesting and important observation recently made by my assistant, Mr. E. O. Brown, in connexion with gun-cotton. The fact that the violent explosion of this substance cannot be developed except when it is confined in receptacles of some strength has been up to the present time accepted as indisputable. It occurred, however, to Mr. Brown that as gun-cotton is analogous in its nature and operation as an explosive agent to nitroglycerin, differing principally from that substance in the rapidity and consequent violence of its explosion, it might also, like nitroglycerin, be susceptible of violent explosion when unconfined, by being ignited through the agency of detonation. This proved to be the case; for upon exploding a small charge of detonating powder in contact with, or in the immediate vicinity to, compressed gun-cotton freely exposed to air, instead of the latter being simply inflamed and then burning gradually, as would be the case if it were brought into contact with flame or any sufficient source of heat, it explodes with great violence, exerting a destructive action equal to that of nitroglycerin, and decidedly greater than that produced by gun-cotton when exploded under the conditions hitherto believed to be those most favourable to the full development of its explosive force. The explosion of a small mass of compressed gun-cotton in this manner suffices to determine the similarly violent and apparently simultaneous explosion of small detached masses of the same material, which may indeed be placed at distances of 0·5 to 1 inch from the original source of the explosion or from each other. Thus, rows of detached masses of gun-cotton, placed on the ground, and extending 4 or 5 feet, have been exploded with most destructive results, by the firing of a small detonating tube in contact with the piece of compressed gun-cotton which formed one extremity of the row or train, the explosion of the entire quantity being apparently instantaneous and equally violent throughout.

In the first experiments instituted with the view of ascertaining the conditions to be fulfilled for ensuring the development of

the violent action, or for accomplishing the detonation of gun-cotton when perfectly unconfined, the following points were observed:—

1. If a confined charge of mercuric fulminate be placed in contact with, or buried in gun-cotton which is in the form of wool or spun-yarn, its explosion does not develope the violent action of the gun-cotton, as would be the case if the latter were in the form of a compact, hard, and homogeneous mass (as obtained by submitting finely divided gun-cotton to powerful pressure). The light and loose gun-cotton is simply scattered with violence; portions of it are sometimes ignited by the flame of the exploding fulminate, the latter result being obtained with greater certainty, the less violent the detonation produced by the fulminate-charge.

2. The detonation of a small mass of compressed gun-cotton, freely exposed to air, by means of a mercuric fulminate-charge, does not accomplish the explosion of light gun-cotton wool or yarn placed in immediate contact with it; the latter is scattered and partially inflamed, as in the preceding case.

3. If the detonation of the fulminate-charge which is placed in contact with a mass of compressed gun-cotton is not sufficiently violent or sharp to effect the explosion, the solid mass is shattered and violently dispersed; if the detonation is upon the verge of that required for determining the violent explosion of the gun-cotton, no inflammation of the latter takes place; but if the explosion of the fulminate-charge is comparatively feeble, portions of the gun-cotton are inflamed at the moment of dispersion of the mass.

4. Explosive substances which are inferior to mercuric fulminate in the suddenness and consequent momentary violence of their detonation, cannot be relied upon to effect the violent explosion of freely exposed gun-cotton, even if employed in comparatively considerable quantities. Thus, even ordinary percussion cap composition, which consists of a mixture of mercuric fulminate and potassic chlorate, cannot be used for the detonation of freely exposed gun-cotton, unless a much more considerable amount be used than is necessary of pure mercuric fulminate for that purpose. Many other detonating mixtures, exploding less rapidly and violently than the above, have been tried without success in very considerable quantities, as agents for developing the detonation of gun-cotton in open air.

5. The quantity of confined mercuric fulminate required to effect the detonation of freely-exposed gun-cotton, is regulated by the degree to which the sharpness of its explosion is increased by the extent of accumulation of force, consequent upon the strength of envelope in which the fulminate is confined. From 1·3 to 2·0 grms. (20 to 30 grains) are required to detonate the gun-cotton, if the fulminate be confined in a thin case of wood, or in several wrappings of paper, while the same result can be produced with 0·32 grm. (5 grains) if that amount be confined in a cap of thin sheet metal.

If the fulminate be placed in a wide paper cylinder open at the top, which is rested upon the gun-cotton surface, or if it be placed in a heap directly upon the surface of gun-cotton, and if in either instance the violent explosion of the fulminate be effected through the agency of a platinum-wire placed at the *base* of the heap, about 2 grms. (25 to 30 grains) of fulminate will also accomplish the detonation of the gun-cotton, the violent action of the fulminate being, in these instances, developed by the confinement of the portions first ignited in a weak envelope, which consists partly or entirely of the surrounding or superincumbent fulminate.

6. It need perhaps scarcely be stated that the degree of proximity of the detonating charge to the gun-cotton, which is essential for the explosion of the latter, is regulated by the violence of the detonation produced. 0·32 grm. (5 grains) of fulminate enclosed in a metal cap must be placed in close contact with (*i.e.*, closely surrounded by) the unconfined gun-cotton, in order to effect its explosion, while 1·3 grm. (20 grains), similarly confined, will produce the same result if placed at least 0·5 inch distant from the surface of the compressed gun-cotton.

The foregoing facts appear to point to the mechanical action of a detonation as being the real cause of the violent explosion of freely exposed gun-cotton or nitroglycerin. At any rate they appear to indicate decisively that such explosion is not a result of the direct application of the heat developed by the explosion of the detonating materials. If it were so, then the detonating mixture described as percussion-cap composition, and other explosive mixtures, the ignition of which is attended by much greater development of heat than is obtained by the ignition of pure mercuric fulminate, should explode freely ex-

posed gun-cotton more readily than the latter does; the readiness with which the gun-cotton is exploded should be solely proportionate to the amount of fulminate employed; and gun-cotton should be more readily exploded in the loose and open condition than in the compact and highly compressed form; for the latter presents it in the condition least favourable, and the former that most favourable to ready and rapid ignition by heat. Again, the actual temperature required for the explosion of nitroglycerin is very considerably higher than the exploding temperature of gun-cotton; the former may be heated to a temperature of 193° C. (380° F.) for some time without exploding, while the latter inflames at a temperature of 150° C., yet a much smaller charge (not more than 0·2 of the amount) of fulminate suffices for the explosion of unconfined nitroglycerin than is needed for the detonation of gun-cotton. On the other hand, a quantity of confined percussion-cap composition which, if it were pure mercuric fulminate, would be altogether inadequate for the detonation of gun-cotton, suffices for the detonation of nitroglycerin.

Although the foregoing facts appear to afford indisputable evidence that the direct application of heat, from an exploding charge of detonating powder, is not concerned in developing the violent action of gun-cotton or nitroglycerin, an attempt has been made to devise some experiments in which the detonation of either of those substances by the agency described should be accomplished in such a manner as to interpose an effectual barrier between the material to be exploded and the heated gases or flame resulting from the ignition of the charge of fulminate destined to furnish the initiative detonation.

Some small pellets of compressed gun-cotton saturated with nitroglycerin were placed in a cylindrical wooden case open at one end and fixed at the bottom of a trough of water; the air-spaces between the separate pellets were thus occupied by water, the height of which above the charge was about one foot. An electric fuse, primed with 2·6 grms. (40 grains) of mercuric fulminate was weighted and placed at the bottom of the trough, on one side of the cylinder, and at a distance of 2 inches from it. The detonation of the fulminate did not explode the charge; the experiment was then repeated, the water-space which intervened between the fuse and the wooden cylinder being reduced to 1 inch. In this instance the firing

of the fuse exploded the immersed pellets, the water was projected to a great height, the trough was broken into small fragments, and a crater was formed in the ground upon which it rested. This experiment was repeated with the same results. A small cylinder of compressed gun-cotton saturated with nitroglycerin, was enclosed in a paper case, which was thickly coated with a gutta-percha and pitch cement. A screen of thin sheet copper was placed at the bottom of a trough, and the waterproofed charge of explosive material was weighted and placed upon one side of the screen at 0·25 inch distance from it. A waterproofed electric fuse primed with 2·6 grms. (40 grains) of mercuric fulminate was placed on the other side of the screen at a distance of 1 inch from the latter; the trough was then filled with water, so that the screen, charge, and fuse were each surrounded and separated by the liquid. In the first experiment, the explosion of the fuse did not affect the charge, but upon repeating the experiment with a fuse placed at a distance of 0·75 inch from the screen, the charge was violently exploded, as in the former experiment.

A precisely similar experiment was tried with cylinders consisting of compressed gun-cotton only, and enveloped in coatings of some thickness of the gutta-percha cement; but even when the charge and the fuse were placed close to the sides of the screen which separated them under water, the gun-cotton was not exploded by the detonation of the fulminate; the same negative result was obtained when a fuse (enveloped in the waterproof coating) was placed immediately upon a gun-cotton charge enclosed in the paper case and waterproof cement, and exploded under water or in open air. These negative results were instructive, as indicating that the thick yielding envelope which enclosed the gun-cotton charge (possibly assisted by the thin air-cushion by which the enclosed charge was also surrounded) served to protect the comparatively less sensitive explosive material, gun-cotton, by reducing or absorbing the power of the blow or concussion (or whatever the disturbing impulse may be). This explanation was shown to be correct by the fact that a cylinder of gun-cotton, enclosed in a water-tight case of thin sheet metal, and immersed in water, was violently exploded by a fulminate-fuse which was placed by its side, with about 0·25 inch of intervening water.

Some nitroglycerin, contained in a glass beaker, placed at

the bottom of a trough filled with water, was not exploded by a fulminate-fuze, placed at a distance of two inches from the side of the beaker; but when the intervening water was reduced to little more than one inch, the detonation of the fuse exploded the nitroglycerin.

A 12-pounder cast-iron shell was filled about one-half with small granules of gun-cotton impregnated with nitroglycerin; it was then filled with water, and a waterproof fulminate-fuse was inserted through the plug which closed the shell. The fuse and each separate granule of the explosive agent were therefore surrounded by water. Upon ignition of the fuse, the shell (which was placed in a very strong room) exploded with a violent report, and was broken into very small fragments, the greater number of which were buried in the timber which lined the cell. A similar shell was half filled with the same explosive agent; the spaces between the granules and the empty portion of the shell were then filled with a thin plaster of Paris mixture, and a fulminate-fuse was imbedded in the solid plaster which filled the upper half of the shell. The explosion of the fuse was attended by a precisely similar result to that obtained in the preceding experiment.

It is believed that these experiments, together with the facts regarding the behaviour of gun-cotton which have been stated in the earlier part of this paper, afford convincing proof that the violent explosion of gun-cotton and nitroglycerin through the agency of a detonating fuse, must be ascribed either to the mechanical effect of that detonation (*i.e.*, to the work done upon the particles more immediately exposed to the blow or concussion of the detonation), or to the development of a disturbance of chemical equilibrium in the explosive agent by the suddenness and peculiar character of the concussion, or by the powerful vibrating impulse which the detonation establishes.

The readiness and certainty with which gunpowder, gun-cotton, and other explosive substances may be detonated through the agency of a blow from a hammer or a falling body, are regulated by several circumstances; they are in direct proportion to the weight of the falling body, to the height of its fall, or the force with which it is impelled downwards, to the velocity of its motion, to the mass and rigidity, or hardness, of the support or anvil upon which the body falls; to the quantity and mechanical condition of the explosive agent struck, and to

the ready explosibility of the latter. Thus a sharp blow from a small hammer upon an iron surface will detonate gunpowder with very much greater certainty than the simple fall of a heavy hammer, or than a comparatively weak blow from the latter. It is very difficult, by repeated blows applied at very brief intervals, to ignite gun-cotton, if placed upon a support of wood or lead, both of which materials yield to the blow, the force set into operation by that blow being transferred through the explosive agent and absorbed in work done upon the material composing the support. If, however, the latter be of iron, which does not yield permanently to the blow of the hammer, the detonation of these substances is readily accomplished. If the quantity of explosive agent employed be so considerable as to form a thick layer between the hammer and support, the force applied appears to be to so great an extent absorbed in the motion imparted to the particles of the compressible mass, that its explosion is not readily accomplished; and if the material be in a loose or porous condition (as, for example, in a state of powder or of loose wool), much work has to be accomplished in moving particles of the mass through a comparatively considerable space, and a second or even third blow is therefore required to determine its explosion.

These circumstances would appear to afford support for the belief that the detonation of an explosive material through the agency of a blow is the result of the development of heat, sufficient to establish energetic chemical change, by the expenditure of force in the compression of the material, or by the friction of the particles against each other, consequent upon a motion being momentarily imparted to them. It is conceivable that, from either of these causes, sufficient heat may be accumulated with almost instantaneous rapidity, in some portion of the mass struck, to develope sudden chemical change. The circumstance, that the detonation of those portions of an explosive compound (such as gun-cotton or nitroglycerin) which are immediately between the surfaces of the hammer and the support is not communicated to the surrounding portions, may be ascribed to a combination of two causes, the instantaneous nature of the explosion, and the close confinement of the portions struck at the instant of their explosion. The mechanical effect of the detonation is absorbed by the masses of metal between which it occurred, and the gases developed disperse

the surrounding portions of the explosive agent, as they rush away from between the two surfaces.

The exceedingly violent motion of particles resulting from the sudden or extremely rapid transformation of a solid or liquid explosive body into highly expanded gas or vapour, must obviously exert a force which operates upon a resisting body, in the vicinity, in a manner precisely similar to the force applied by opposing a body in the path of a solid mass which is set into very rapid motion. In other words, a detonation exerts a mechanical effect upon resisting bodies precisely similar to that of a blow, as from a falling hammer or a projectile propelled from a gun. Just as the force of a sufficiently sudden or powerful blow from a hammer is transformed into heat by the resistance to the motion of the hammer which the particles of an opposing body present, and by the consequent friction established between those particles, so the force or concussive action exerted by the matter set in motion when a solid or liquid is converted into gas or vapour, will also be transformed into heat, the development of which in an opposing body will be proportionate to the resistance to motion which its particles offer, and to the suddenness and violence of the concussion to which it is subjected.

The power of accomplishing the explosion or detonation of gun-cotton or nitroglycerin in open air through the agency of a detonation produced in its vicinity, would therefore appear to be correctly ascribable to the heat suddenly developed in some portion of the mass by the mechanical effect, or blow, exerted by that detonation, and would seem to be regulated by the violence and suddenness (either singly or combined) of the detonation, by the extent to which the explosive material is in a condition to oppose resistance to the force, and by the degree of sensitiveness of the substance to explosion by percussion.

The following points appear to support this view :—

1. Explosive mixtures (such as percussion-cap composition, and mixtures of potassic chlorate with potassic picrate, &c.) which are apparently but little inferior to the fulminate in the rapidity of their explosive powers, will not detonate freely exposed gun-cotton even though confined charges of them, amounting to about ten times the quantity of mercuric fulminate required to produce the effect with perfect certainty, are employed.

2. On the other hand, nitroglycerin, which is much more readily exploded by a blow than gun-cotton, may be detonated through the agency of explosive mixtures less violent and sudden in their action than the fulminate. A quantity of percussion-cap composition, about one-half that of the minimum of fulminate required to detonate gun-cotton, will suffice to detonate nitroglycerin.

3. If the suddenness of the detonation produced by means of mercuric fulminate be increased by its confinement in a strong envelope, a very much smaller quantity suffices to develope the detonation of gun-cotton than if the fulminate be exploded in open air, or in an envelope which offers but slight initial resistance.

4. The mechanical condition of the gun-cotton most materially influences the result obtained by its exposure to detonation, as has already been shown.

There are, however, several well-known facts, and some results of experiments instituted with special reference to this subject, which do not appear to be in harmony with the assumption that the detonation of nitroglycerin and gun-cotton in the manner described is simply due to the *suddenness* of the development and application of physical force. The following are some of the more important facts of this kind:—

1. The circumstance that the explosion of mercuric fulminate accomplished the detonation of gun-cotton, whereas explosive agents less sudden in their action failed to furnish this result, appeared to render it probable that silver fulminate, which explodes more suddenly and with much more powerful local force when applied under the same conditions, would accomplish the detonation of gun-cotton more readily than the mercury compound, *i.e.*, it was anticipated that a larger amount of the latter would be needed, than of silver fulminate, to produce the desired effect. This proved, however, not to be the case. The minimum quantity of mercuric fulminate which can be relied upon to detonate compressed gun-cotton is 0·324 grm. (5 grains), and it is necessary to enclose that quantity in a case of stout sheet metal, and to place it in close contact with the gun-cotton in order to obtain the desired result. 0·324 grm. (5 grains) of silver fulminate enclosed in tin-foil, though it appeared to produce quite as sharp a detonation as the corresponding quantity of mercury salt confined in the stout case,

did not explode gun-cotton with which it was closely surrounded, but merely shattered and dispersed the mass. But when enclosed in the stout sheet-metal cap, the 0·3 grm. of silver fulminate accomplished the detonation of gun-cotton.

2. Iodide of nitrogen, as one of the most sensitive and, apparently, violently explosive compounds with which we are acquainted, was next experimented with. The susceptibility to sudden explosion even of silver fulminate will not bear comparison with that of the iodide of nitrogen or of the corresponding chlorine compound, though, as regards the mechanical effect of the explosion (*i.e.*, its local destructive action) both of those compounds accomplished decidedly less work than the silver-fulminate under the same conditions.

Many unsuccessful attempts have been made to explode gun-cotton through the agency of iodide of nitrogen. Pellets of this substance (weighing about 0·2 grm. and 0·35 grm.), resting upon paper or thin cardboard, were carefully placed, when perfectly dry, upon compressed gun-cotton, and were then exploded by being touched with the end of a long rod; the compact masses of gun-cotton were more or less disintegrated by the explosions, but no detonation resulted. Indications having been obtained that the violence of explosion of the iodide was decidedly increased by its confinement, two descriptions of small shells charged with the substance were prepared. About 1 grm. of the iodide was placed, while moist, in a small cup of plaster of Paris, a spherical mass of the plaster was then formed round this, so that after a time the explosive agent was enclosed in a hard shell, the walls of which were about 0·3 inch in thickness. The shells thus produced were confined for several days in proximity to a desiccating agent, until the perfect desiccation of the iodide of nitrogen through the porous plaster shell had been accomplished; they were then allowed to fall from heights of 4 feet and 20 feet upon masses of compressed gun-cotton; their explosion simply shattered the latter. Similarly negative results were obtained with corresponding quantities of the iodide confined in small cases of stout sheet copper. 6·5 grms. (100 grains) of iodide of nitrogen were also exploded in direct contact with compressed gun-cotton, without accomplishing its detonation.

3. The following experiments were made with chloride of nitrogen, for the purpose of comparing its power to accomplish

the detonation of gun-cotton with that of the explosive agents already discussed. About 0·65 grm. (10 grains) of the chloride were transferred to a thin watch-glass and covered with a film of water: the watch-glass was placed upon a pellet of gun-cotton which rested upon the ground. The chloride of nitrogen was then exploded by means of a long rod, the extremity of which was moistened with turpentine. The glass was shattered and dispersed, but the mass of gun-cotton was only to a slight extent disintegrated. 1 grm. of the chloride was next employed in precisely the same manner; the gun-cotton pellet was not exploded, but was much shattered by the explosion. About 2 grms. (31 grains) of the chloride, applied as before, did not explode the gun-cotton, but the pellet was completely broken and violently scattered. 3·25 grms. (50 grains) of the chloride were next employed; in this instance the gun-cotton was detonated by the explosion of the liquid. The experiment was repeated with what was estimated to be the same quantity of chloride of nitrogen; the gun-cotton pellet was not exploded, but was completely disintegrated and scattered, the effect being the same as that produced with an amount of mercuric fulminate just below that required to accomplish the detonation of gun-cotton. It would appear therefore that 3·25 grms. (50 grains) of chloride of nitrogen, covered with water is about the minimum quantity required to accomplish the result attainable with 0·32 grm. of mercuric fulminate enclosed in a metal case.

The foregoing results obviously do not support the view that the suddenness or sharpness of a detonation alone favours the development of violent explosive force from gun-cotton in open air. The silver-fulminate produces a much sharper explosion than the mercuric fulminate, yet it was not found that a smaller quantity of the former than of the latter was required for the detonation of gun-cotton. The explosion of the iodide and the chloride of nitrogen is certainly more sudden than that of the above fulminates, unconfined, and at any rate equally so with the confined fulminates; yet it was not found possible to detonate gun-cotton by the explosion of 6·5 grms. (100 grains) of the iodide, in contact with it, and 3·24 grms. (50 grains) of chloride of nitrogen, *confined by water*, were required to accomplish the result attained by 0·32 grm. of either of the confined fulminates

or by 2 grms. of the mercuric fulminate, unconfined by any strong envelope.

With the view of ascertaining whether the relative power of different explosive agents to accomplish the detonation of gun-cotton appears to be in direct proportion to the relative mechanical effects of their explosion (*i.e.*, to the work performed by them upon a body placed in contact with them), a series of experiments was instituted with the object of comparing this particular action of the several explosive materials.

A thin and uniform copper sheet was cut up into square pieces of equal dimensions, and these were similarly supported at their corners only. Equal quantities of the four different explosive agents, the mercury- and silver-fulminates and the chloride and iodide of nitrogen, were employed. In some experiments the fulminates were placed in direct contact with the copper, in others, with the view of comparing them accurately with the iodide of nitrogen, they were placed upon thin cards which rested upon the sheet copper. The iodide of nitrogen was always used in this way, but as for obvious reasons the chloride of nitrogen could not be thus employed, it was placed in very thin watch-glasses, which rested upon the copper sheet.

The following is a summary of the results furnished by repeated experiments with a series of different proportions of the several explosive agents.

The violence of explosion of chloride of nitrogen, when unconfined, is less than that of the iodide; if confined under water, it very considerably exceeds that of the exposed iodide, but falls very short of that exerted by unconfined silver-fulminate. The mercuric fulminate, which is much less rapidly explosive than either of the other substances, exerts less mechanical force than any of them, if freely open to air, and if inflamed at some portion of the exposed surfaces; if ignited at the lower inner portion of the mass, where the part first inflamed is enclosed by the mass of the material itself, it exerts a destructive force little inferior to that of the chloride of nitrogen enclosed by water; but if confined in a strong envelope (*e.g.*, of sheet tin), the mercuric fulminate exceeds the unconfined silver fulminate in violence of action.

These results to a great extent confirm the correctness of the view that the readiness with which the detonation of gun-cotton

is accomplished is in proportion to the mechanical force exerted by the initiative detonation to which it is subjected. The force exerted by small quantities of strongly confined silver- and mercuric-fulminate greatly exceeds that developed by the explosion of comparatively large proportions of the iodide and chloride of nitrogen. This may be accepted as accounting, to some extent, for the fact that the detonation of gun-cotton could not be accomplished by an amount of iodide of nitrogen twenty times greater than that of fulminates required for the purpose, while ten times the quantity of the confined chloride were required to produce the result. That the quantity of mercuric fulminate required to produce detonation is reduced in proportion as means are applied to increase the violence of the force exerted by it at one time, is quite in accordance with the above view.

Several curious and apparently anomalous effects were, however, observed in the course of the numerous experiments referred to in this paper, which suggest the inquiry whether there may not be some peculiarity in the concussion or powerful vibration produced by a particular kind of explosion, which acts apart or distinct from the mechanical force of that explosion in developing or promoting the detonation or sudden chemical disintegration of the molecules of a neighbouring explosive body.

The results of a few experiments instituted with nitroglycerin appear to furnish a decided affirmative reply to that inquiry. A comparison was in the first instance instituted between the mechanical action of the explosion of nitroglycerin, and of the other materials which have been discussed. The charges of nitroglycerin were introduced into small wide tin tubes, freely open at the upper end or closed by means of a cement, and their explosion was accomplished by the detonation of a small percussion-cap, just immersed in or resting upon the liquid, and containing 0·07 grm. (1 grain) of mercuric fulminate. Nitroglycerin thus detonated produced a destructive effect upon the copper support very greatly exceeding that obtained with the same amount of unconfined silver-fulminate. As the mechanical force developed by nitroglycerin was so very considerable, and as, moreover, the character of its detonation might be expected to bear some analogy to that of gun-cotton, it was considered probable that the latter might prove susceptible of detonation by a much smaller proportion of nitroglycerin

than it is necessary to employ of the confined fulminates. No success, however, attended repeated attempts to explode gun-cotton by the detonation of 0·07 grm. (1 grain) and increasing charges up to 0·65 grm. (10 grains) of nitroglycerin. At the same time these results were not quite conclusive, as it was not found easy to ensure the complete detonation of the liquid by the small fulminate-charge, on account of the difficulty of securing a favourable adjustment of the detonating cap and the very small quantity (from two to ten drops) of nitroglycerin used. The experiments were therefore repeated with corresponding quantities of the liquid converted into a thick paste by admixture with sand, in tin tubes similar to those previously used. The explosion of the nitroglycerin appeared to be rendered more certain by this contrivance, but in order more thoroughly to ensure its proper detonation, the charge of mercuric fulminate used for that purpose was increased to 0·14 grm. (2 grains). Still the detonation of gun-cotton could not be accomplished, although the charge of nitroglycerin was gradually increased to 1 grm. The disc of compressed gun-cotton, which rested upon a support of wood, was shattered almost to dust, portions being driven deeply into the wood, which exhibited an indentation corresponding to the form of the disc. In order to compare the mechanical effect of the detonation of nitroglycerin with that of the strongly confined fulminates, 0·65 grm. (10 grains) of the liquid were placed in the small tin tube upon stout sheet copper and detonated by means of 0·14 grm. (2 grains) of mercuric fulminate; the work done upon the copper resembled in extent that accomplished with a corresponding charge of the confined fulminate (double the amount required to effect the detonation of gun-cotton). It appeared evident, therefore, that some power, apart from violence of explosion, was wanting in nitroglycerin to produce the result obtained with the fulminate. With a view to obtain still more decided evidence on this point, the experiments were continued upon a larger scale. Some four-ounce discs of compressed gun-cotton were placed upon thick supports of wood, and confined charges of nitroglycerin, weighing about 0·75 ounce and one ounce were placed upon these discs and successively exploded. The pieces of wood were more or less shattered; they were deeply indented (the circumference of the disc being clearly imprinted upon them),

and the gun-cotton was pulverized and violently scattered, portions being driven firmly into the wood, but the desired result was not in any instance accomplished.

In contrast to the foregoing results, it may be mentioned that small perforated cylinders of compressed gun-cotton, weighing 7·75 grms. to 15·5 grms. (0·25 oz. to 0·5 oz.), with the usual small confined charge of mercuric fulminate inserted into the perforation, have frequently been employed, and invariably without failure, for effecting the detonation of a large disc or slab of gun-cotton, or of a number arranged side by side in open air, by simply placing them upon or against any one of the surfaces of the larger mass of gun-cotton. It should also be stated that the detonation of a small quantity of nitroglycerin has been found to accomplish the simultaneous explosion of surrounding charges of that substance closely confined in small vessels of sheet tin, and placed at distances of 2 or 3 inches from the central charge. Lastly, it was found that the detonation of 7·75 grms. (0·95 ounce) of gun-cotton determined the explosion, simultaneously with it, of a charge of nitroglycerin confined in a vessel of sheet tin, and placed at a distance of 1 inch from the gun-cotton, while 15·5 grms. (0·5 ounce) of the latter produced the same result when separated from the confined nitroglycerin by a space of 3 inches.

The results obtained with nitroglycerin in attempts to detonate gun-cotton through its agency, appear to me to substantiate the view which has obtruded itself repeatedly on my mind upon consideration of many of the phenomena observed in the experiments detailed in this communication, namely, that a particular explosion or detonation may possess a power of determining at the instant of its occurrence similarly violent explosions in distinct masses of the same material, or in contiguous explosive bodies of other kinds, which power is independent of, or auxiliary to, the direct operation of mechanical force developed by that explosion; that, as a particular musical vibration will establish synchronous vibrations in particular bodies while it will not affect others, and as a chemical change may be wrought in a body by its interception of only particular waves of light, so some kinds of explosions or powerful vibratory impulses may exert a disturbing influence over the chemical equilibrium of certain bodies, resulting in their sudden disintegration, which other explosions, though developing equal or greater mechanical

force, are powerless to exercise. Thus the mechanical force developed by the explosion of 3·25 grms. (50 grains) of chloride of nitrogen far exceeds that exerted by the explosion of 0·32 grm. (5 grains) of the strongly confined fulminates, yet, in their effects upon gun-cotton, the substances in question are not on an equality unless employed in about those proportions. It appears, therefore, that it is necessary to increase greatly the mechanical force of the explosion to obtain the desired result with chloride of nitrogen, in order to compensate for the deficiency or absence of some peculiar power possessed by the explosion of the fulminates. Again, in the case of nitroglycerin, we have a body which explodes with a development of force quite as great as that of the strongly confined fulminates, yet the detonation of gun-cotton could not be accomplished by the explosion in close contact with it of a quantity of nitroglycerin more than sixty-five times greater than the amount of mercuric or silver-fulminate required for that purpose.

I venture to offer the following as being the most satisfactory explanation which occurs to me of the remarkable differences just pointed out in the behaviour of different explosive agents. The vibrations produced by a particular explosion, if synchronous with those which would result from the explosion of a neighbouring substance which is in a state of high chemical tension, will, by their tendency to develope those vibrations, either determine the explosion of that substance, or at any rate greatly aid the disturbing effect of mechanical force suddenly applied, while, in the case of another explosion which produces vibrations of different character, the mechanical force applied by its agency has to operate with little or no aid; greater force or a more powerful detonation must, therefore, be applied in the latter instance, if the explosion of the same substance is to be accomplished by it.

The power possessed by the violent explosion of a particular material (such as gun-cotton or nitroglycerin) to determine the apparently simultaneous explosion of perfectly separate masses of the same substance, does not excite surprise. Instances of the apparently simultaneous explosion of numerous distinct and even somewhat widely separated masses of explosive substances (such as simultaneous explosions in several distinct buildings at powder-mills) do not unfrequently occur, in which the generation of a disruptive impulse by the first or initiative

explosion, which is communicated with extreme rapidity to contiguous masses of the same nature, appears much more likely to be the operating cause, than that the simultaneous explosion should be brought about by the direct operation of heat and mechanical force developed by the starting explosion.

It appears remarkable that two substances so analogous as gun-cotton and nitroglycerin in their chemical constitution and general characters as explosive agents, should exhibit the very great differences which have been observed in their susceptibility to explosion by the effects of a detonation. A comparatively very small amount of mechanical force, suddenly applied, suffices to develope the violent decomposition of nitroglycerin; it is therefore not difficult to understand why this substance, though incapable of detonating gun-cotton, even when used in considerable quantities, should be itself readily exploded by means of the latter. The comparatively very great sensitiveness of nitroglycerin to explosion through the agency of a detonation may probably be due in part to its physical character as a liquid, and in part to the fact that the proportion of oxygen to oxidisable elements is much more considerable in nitroglycerin than in gun-cotton.

In considering the manner in which a detonation operates in determining the violent explosion of gun-cotton and nitroglycerin in open air, I have, for the sake of simplicity, confined myself to an examination of the manner in which those particular explosive substances are affected by the disturbing agency in question. It must not, however, be supposed that the power to exert a violent explosive action, when unconfined or partly exposed to air, is limited to explosive *compounds*. A few experiments instituted with explosive *mixtures* (produced by the intimate incorporation of powerful oxidising agents and readily oxidisable substances, the combustion of which furnishes gases or vapours) have demonstrated that the destructive or explosive force of these may also be fully developed under conditions most unfavourable to their operation as explosive agents, under ordinary circumstances, if they are submitted to the influence of *a detonation*. Mixtures of potassic chloride with the sulphides of antimony or arsenic, with potassic ferro- or ferri-cyanide, with potassic picrate, and other explosive mixtures of similar nature, and lastly even gunpowder, have been readily made to

explode, when unconfined, with the full force which they are capable of exerting, by being placed in contact with a confined charge of mercuric fulminate. As far as could be determined by small comparative experiments, the readiness with which the violent explosion of these mixtures can be developed, is in direct proportion to their sensitiveness to explosion by percussion. Thus a mixture of the potassic picrate and chlorate, freely exposed to air, is exploded apparently with as much facility as gun-cotton by the detonation of a small fulminate-charge, and the violence of the explosion approaches that of gun-cotton fired under the same conditions. The detonation of a freely exposed mixture of the chlorate with sulphide of antimony is somewhat less readily accomplished, and the violent explosion of gunpowder requires the fulfilment of special conditions favourable to the action of the detonating charge of fulminate. If a small charge of powder be merely heaped upon a flat surface, the case which contains the fulminate being inserted into the heap, the grains are simply scattered by the detonation of the fulminate; but if a corresponding quantity of gunpowder be so arranged that the dispersion of the grains is impeded (as by placing it in a cylinder quite open at the upper end), its violent explosion is accomplished with certainty.

The results of a few experiments instituted with small charges of gunpowder (8 ozs. and 1 lb.) appeared to furnish decisive indications that their explosion through the agency of a detonation was considerably more rapid than when flame was applied or their ignition under corresponding conditions. The charges were enclosed in sheet-tin cases closely resembling each other, which were buried in the ground under precisely similar conditions. Those charges which were exploded by the ordinary electric fuses, produced clear holes, the earth being partly piled up around, and partly scattered; others, fired by means of detonating fuses, threw up much earth vertically with considerable violence, but there was very little scattering effect produced, the hole being to a great extent filled up again by the earth momentarily displaced.

That the explosion of gun-cotton through the agency of detonation exerts a more violently destructive action than its explosion when strongly confined, by the simple agency of heat, has been abundantly proved by blasting operations in

various descriptions of rock, and by measurement of the comparative destructive effect of charges exploded under water. Charges of gun-cotton contained in blast-holes, and having a detonating fuse inserted in or placed immediately over them, have produced much greater rending and shattering effects in hard rock and in wood (although the blast-holes were left entirely open, or only filled with loose sand, earth, or powdered rock) than corresponding charges applied in similar positions, but fired with ordinary fuses, although in the latter instances the gun-cotton was confined by "tamping," or firmly closing the blast-hole to a considerable depth. A series of systematic experiments have been carried on at Chatham by the Government Committee on Floating Obstructions, with the view of comparing the destructive power of gunpowder and gun-cotton, in which charges of these materials were exploded in proximity to submerged targets, with systematic variations of the strength of the cases containing the charges, the depth of their immersion beneath the surface, and their distances from the targets. The results of these experiments warranted the conclusion that gun-cotton, when confined in cases of sufficient strength to develope its full explosive action, exerted a destructive effect equal to about five times that of gunpowder. A few experiments to compare with these have been recently instituted with charges of gun-cotton enclosed in thin sheet-metal cases and exploded by means of detonating fuses, and in these the destructive action upon vertical targets, placed at very considerable distances from the charges, was from ten to twelve times greater than that of gunpowder. The concussion imparted through the water to considerable distances, by the explosion of small charges (2 to 3 lb.) of gun-cotton in the new manner, very greatly exceeded in their effects the results produced by the explosion of submerged charges by the ordinary method.

A series of experiments has been instituted with the object of ascertaining whether the remarkable results obtained by exploding gun-cotton through the agency of a detonation were in any way ascribable to a peculiarity in the results of the metamorphosis. Known weights of gun-cotton have been exploded *in vacuo* by means of a small detonating fuse, and the volume of gas produced accurately determined. After deducting the volume furnished by the fuse employed, the results obtained corresponded very closely to those furnished by ex-

ploding shells, charged with gun-cotton, through the agency of a heated platinum wire, under precisely similar conditions. The products of explosion of the detonated gun-cotton have been submitted to complete analysis, and the results did not differ in any very important respect from those obtained by the most complete metamorphosis of the substance when exploded in strong shells under ordinary conditions. As the chemical change sustained by the decomposition of gun-cotton, when exploded through the agency of a detonation, cannot be said to differ in completeness from that consequent upon a fulfilment of the ordinary conditions essential to the development of its full explosive force, the increased destructive effect developed by the explosion of gun-cotton through the agency of a detonation must obviously be ascribed to the greater rapidity of its explosion under these conditions. This conclusion appears to receive confirmation from some of the results of a series of practical blasting operations which I have recently conducted at Allenheads, in conjunction with Thomas Sopwith, M.A., F.R.S., from which it appeared that, while the splitting and shattering effects upon hard rock were much greater with "detonated" gun-cotton than with charges of this material exploded in the ordinary way, the displacement or projection of the broken rock appeared decidedly less considerable. Again, the work accomplished in the way of displacement in a comparatively soft and yielding material, such as a very friable rock (*e.g.*, chalk or soft limestone), is less considerable than when the more gradual explosion of gun-cotton is brought about by the usual mode of firing. In the case of the detonation of gun-cotton imbedded in such material, the force which is applied with comparative suddenness is to a considerable extent expended in the disintegration and compression of the surrounding material, before there is time for motion to be communicated through any considerable mass of the rock. A further indication of the difference in the rapidity of explosion of gun-cotton by detonation and by the simple application of heat is furnished by the difference in the luminous effect observed in the two instances. The ordinary explosion of gun-cotton is attended by a considerable body of flame, due to the ignition of the generated carbonic oxide; but the detonation of gun-cotton is only attended by a sudden flash, which it is very difficult to observe in daylight if only small quantities are ex-

ploded. The transformation of the solid into gas appears, in fact, to be too sudden for the generated combustible gas to become inflamed.

In conclusion, it may not be out of place to refer briefly to a few illustrations of the important bearings which the new mode of developing the explosive force of gun-cotton has upon the practical uses of the material as a destructive agent. The confinement of a charge of gunpowder or gun-cotton in a blast-hole, by firmly closing up the latter with earth, powdered rock, or other compressible material (by the process known as tamping or stemming) to a depth greater than the line of least resistance opposed to the action of the charge, is essential to the success of a blasting operation; but the great rapidity of explosion, by detonation, of a charge of gun-cotton greatly reduces the value of this operation; the destructive effect of the material, when exploded in a hole which is left open, is not inferior in extent to that obtained by similarly exploding a charge confined in the usual manner. Thus the most dangerous operation in connexion with blasting may be entirely dispensed with.* In submarine operations, it is no longer necessary to enclose the charge of explosive agent in the strong and therefore cumbersome metal receptacles hitherto required to ensure the full development of its explosive force; the destructive action of a charge of gun-cotton, enclosed in a waterproof bag or thin glass vessel and exploded by detonation, being decidedly greater than that furnished by a corresponding charge confined in a strong iron vessel and exploded by flame. Small charges of gun-cotton simply resting upon the upper surfaces, or loosely inserted into natural cavities, of very large masses of the hardest description of rock or of iron, have broken these up as effectually as if corresponding charges had been firmly embedded in the centre of the mass and exploded in the usual manner. Lastly, the certainty, facility, and expedition with which certain important military destructive operations may be accomplished by means of gun-cotton exploded by detonation, are not among the least important advantages which are now secured to this interesting and remarkable explosive agent.

* This observation does not apply equally to large charges, such as are used in some military operations, for the placing of which it is necessary to sink or drive shafts or openings of large dimensions.

X.—*Note on the Absorption of Mixed Vapours by Charcoal.*

By John Hunter, M.A., F.C.S., Chemical Assistant, Queen's College, Belfast.

(Read January 20, 1870.)

The results obtained by absorbing a mixture of two vapours by means of cocoa-nut charcoal were published in the "Journal of the Chemical Society," May, 1868. It was found that the absorption was greatly increased when one of the vapours was at a temperature near to its point of condensation. Thus, in the case of ethylic alcohol and water, the amount of mixed vapour absorbed changed rapidly according as the proportion of the former to the latter varied from 1 : 1 to 1 : 3, one volume of cocoa-nut charcoal absorbing 187·2 volumes in the first case, and 255·4 volumes in the last case, at the temperature of 100° C. When the experiments were repeated at a temperature considerably above the boiling point of water (about 160° C.), the absorption diminished with the increased proportion of water from 58·1 to 37·6, an effect naturally to be expected when we reflect that alcohol vapour is much more largely absorbed than that of water at this temperature.

It appeared to me that these experiments might be explained as follows:—When a fragment of charcoal is introduced into a mixture of two vapours, the one which is nearest to its point of condensation is absorbed, and this vapour, in its condensed condition in the pores of the charcoal, absorbs the other vapour previously uncondensed. According to this view, we have a succession of condensations going on, the total absorption depending, not merely upon the power which the charcoal has of absorbing the vapours, but on a complex effect, combining the absorption of the first vapour by the charcoal, and then the absorption of the second by the product of the absorption of the first. If this theory is correct, we should have the vapour of water mixed with gaseous ammonia (obtained by heating the solution of the gas in water), much more largely absorbed than either the gas or the water separately. On making a set of experiments with a solution of ammonia of sp. gr. 0·88, I found the absorption enormously increased, the average absorption by one

volume of cocoa-nut charcoal at 100° C. and 706·2 mm. being 313·6 volumes. I conclude, then, that the water-vapour is first condensed in the charcoal, and as this fluid has the power of absorbing ammoniacal gas to a much greater extent than charcoal, we have the gas condensed in the water contained in the pores, and a greatly increased absorption occurs.

The following are the various experiments :—

Vol. absorbed by one vol. of Cocoa-nut Charcoal.	Temp. C°.	Pres. in mm.
316·6	100°	714·5
311·1	„	711·6
316·2	„	694·6
309·4	„	693·1
315·0	„	717·2
Mean 313·6	100·0	706·2

XI.—*On the Continuity of the Gaseous and Liquid States of Matter.*

By Thomas Andrews, M.D., F.R.S., Vice-President of Queen's College, Belfast.

(From the Philosophical Transactions for 1869.)

In 1822 M. Cagniard de la Tour observed that certain liquids, such as ether, alcohol, and water, when heated in hermetically sealed glass tubes, became apparently reduced to vapour in a space from twice to four times the original volume of the liquid. He also made a few numerical determinations of the pressures exerted in these experiments.* In the following year Faraday succeeded in liquefying, by the aid of pressure alone, chlorine and several other bodies known before only in the gaseous form.† A few years later Thilorier obtained solid carbonic acid, and observed that the coefficient of expansion of the liquid for heat is greater than that of any aëriform body.‡ A second memoir by Faraday, published in 1845,

* Annales de Chimie, 2ème série, xxi, pp. 127 and 178; also xxii, p. 410.

† Philosophical Transactions for 1823, pp 160–189.

‡ Annales de Chimie, 2ème série, lx, pp. 427, 432.

greatly extended our knowledge of the effects of cold and pressure on gases.* Regnault has examined with care the absolute change of volume in a few gases when exposed to a pressure of twenty atmospheres, and Pouillet has made some observations on the same subject. The experiments of Natterer have carried this inquiry to the enormous pressure of 2,790 atmospheres; and although his method is not altogether free from objection, the results he obtained are valuable, and deserve more attention than they have hitherto received.†

In 1861 a brief notice appeared of some of my early experiments in this direction. Oxygen, hydrogen, nitrogen, carbonic oxide, and nitric oxide were submitted to greater pressures than had previously been attained, in glass tubes, and while under these pressures they were exposed to the cold of the carbonic acid and ether bath. None of the gases exhibited any appearance of liquefaction, although reduced to less than $\frac{1}{500}$ of their ordinary volume by the combined action of cold and pressure.‡ In the third edition of Miller's "Chemical Physics," published in 1863, a short account, derived from a private letter addressed by me to Dr. Miller, appeared of some new results I had obtained, under certain fixed conditions of pressure and temperature, with carbonic acid. As these results constitute the foundation of the present investigation, and have never been published in a separate form, I may perhaps be permitted to make the following extract from my original communication to Dr. Miller. "On partially liquefying carbonic acid by pressure alone, and gradually raising at the same time the temperature to 88° Fahr., the surface of demarcation between the liquid and gas became fainter, lost its curvature, and at last disappeared. The space was then occupied by a homogeneous fluid, which exhibited, when the pressure was suddenly diminished, or the temperature slightly lowered, a peculiar appearance of moving or flickering striæ throughout its entire mass. At temperatures above 88° no apparent liquefaction of carbonic acid, or separation into two distinct forms of matter, could be effected, even when a pressure of 300 or 400 atmospheres was applied. Nitrous oxide gave analogous results."§

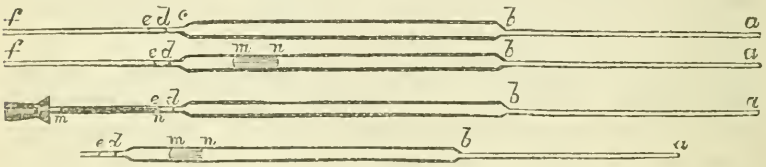
* Philosophical Transactions for 1845, p. 155.

† Poggendorff's Annalen, xciv, p. 436.

‡ Report of the British Association for 1861. Transactions of Sections, p. 76.

§ Miller's Chemical Physics, 3rd edition, p. 328.

The apparatus employed in this investigation is represented in the Plate opposite page 94. It is shown in the simple form in which one gas only is exposed to pressure in Figs. 1 and 2. In Fig. 3, a section of the apparatus is given, and in Fig. 4 another section, with the arrangement for exposing the compressed gas to low degrees of cold *in vacuo*. In Figs. 5 and 6 a compound form of the same apparatus is represented, by means of which two gases may be simultaneously exposed to the same pressure. The gas to be compressed is introduced into a tube ($f\,a$) having a capillary bore from a to b, a diameter of about 2·5 millimetres from b to e, and of 1·25 millimetre from e to f. The gas carefully dried is passed for several hours through the tube open at both ends, as represented below. The presence of a column of water



of two metres in height was necessary to maintain a moderate stream of gas through the fine capillary tube. In the case of carbonic acid, the gas, after passing through the apparatus, was made to bubble by means of a connecting-tube through mercury, and a portion was collected from time to time, in order to ascertain its purity. The current was continued till the residual air, after the action of caustic potash, was reduced to a constant minimum. In repeated trials I found that in the complicated arrangements I had to adopt, the residual air could not be reduced to less than from $\frac{1}{500}$ to $\frac{1}{1000}$ of the entire volume of the carbonic acid. Even after continuing the current for twenty-four hours this residue appeared; and in discussing some of the results obtained by exposing the gas to high pressures the presence of this small quantity of air must be carefully taken into account. The capillary end at a was then sealed, and the other end was also closed, and afterwards introduced under a surface of pure mercury contained in a glass capsule. The lower end, while under the surface of the mercury, was opened, and heat applied so as to expel a little of the gas. On cooling, contraction occurred, and a short column of mercury entered. The capsule and lower end of the tube were then

placed under the receiver of an air-pump, and a partial vacuum was formed till about one-fourth of the gas was removed. On restoring the pressure, a column of mercury entered and occupied the place of the expelled gas. By withdrawing the end of the tube from below the surface of the mercury in the capsule, and again exhausting cautiously, the column of mercury could be reduced to any required length. The tube, when thus filled, had the form shown (Figure, p. 76.).

Two file marks had been made, one at *d*, the other at *e*, in the narrow part of the tube, about 10 millims. distant from each other, and the capacity of the tube from a mark near *a* to *d*, and also from the same mark to *e*, had been determined by filling it with mercury at a known temperature, and weighing the mercury. The tube was now placed accurately in a horizontal position and connected by an air-tight junction with one limb of a long U-tube filled with mercury. Each limb of the U-tube was 600 millims. long, and 11 millims. in diameter. By removing mercury from the outer limb of the U-tube, a partial vacuum was obtained, and the column of mercury (*m n*) was drawn into the narrow tube (*d f*). From the difference of capacity of this part of the tube, the column of mercury was now about four times longer than before. It was easy with a little care so to adjust the pressure that the inner end of the mercurial column coincided with the mark *e*. When this was accomplished, the difference of level of the mercury in the two limbs of the U-tube was accurately read by means of a cathetometer, and the height of the barometer, as well as the temperature, were carefully noted. Similar observations were made with the gas expanded to the mark *d*. Two independent sets of data were thus obtained for calculating the volume of the gas at 0° C. and 760 millims., and the results usually agreed to less than $\frac{1}{1000}$ part. The tube, after being disconnected with the U-tube, was cut across a little beyond *e*, as shown (Figure, p. 76), and was now ready to be introduced into the pressure apparatus.

The capillary tubes were calibrated with great care, and their mean capacity was determined by weighing a column of mercury whose length and position in the tube were accurately observed. One millim. of the air-tube used in these experiments had an average capacity of 0·00002477 cub. centim., and 1 millim. of the carbonic acid tube of 0·00003376 cub. centim. A table was

constructed showing the corrected capacity of each capillary tube from the sealed end for every millimetre of its length. An allowance of 0·5 millim. was made for the cone formed in sealing the tube.

For the sake of clearness I have described these operations as if they were performed in the detached tube. In actual practice, the tube was in the brass end-piece before it was filled with gas (Fig. 7).

The construction of the apparatus employed in these experiments will be readily understood from Figs. 3 and 4, which exhibit a section of the simple form. Two massive brass flanges are firmly attached round the ends of a cold-drawn copper tube of great strength, and by means of these flanges two brass end-pieces can be securely bolted to the ends of the copper tube, and the connections made air-tight by the insertion of leather washers. The lower end-piece (Fig. 7) carries a steel screw, 180 millims. long, 4 millims. in diameter, and with an interval of 0·5 millim. between each thread. The screw is packed with care, and readily holds a pressure of 400 atmospheres or more. A similar end-piece attached to the upper flange, carries the glass tube containing the gas to be compressed (Fig. 7). The apparatus, before being screwed up, is filled with water, and the pressure is obtained by screwing the steel screw into the water.*

In the compound apparatus (Figs. 5 and 6) the internal arrangements are the same as in the simple form. A communication is established between the two sides of the apparatus through *a b*. It is indifferent which of the steel screws below is turned, as the pressure is immediately diffused through the interior of both copper tubes, and applied through the movable columns of mercury to the two gases to be compressed. Two screws are employed for the purpose of giving a greater command of pressure. In Fig. 5 the apparatus is represented without any accessories. In Fig. 6 the same apparatus is shown with the arrangements for maintaining the capillary tubes and the body of the apparatus itself at fixed temperatures. A rectangular brass case, closed before and behind with plate glass, surrounds each capillary tube, and allows it to be main-

* The first apparatus was constructed for me by Mr. J. Cumine, of Belfast, to whose rare mechanical skill and valuable suggestions I have been greatly indebted in the whole course of this difficult investigation.

tained at any required temperature by the flow of a stream of water. In the figure, the arrangement for obtaining a current of heated water in the case of the carbonic acid tube is shown. The body of the apparatus itself, as is shown in the figure, is enclosed in an external vessel of copper, which is filled with water at the temperature of the apartment. This latter arrangement is essential when accurate observations are made.

The temperature of the water surrounding the air-tube was made to coincide, as closely as possible, with that of the apartment, while the temperature of the water surrounding the carbonic acid tube varied in different experiments from 13° C. to 48° C. In the experiments to be described in this communication, the mercury did not come into view in the capillary part of the air-tube till the pressure amounted to about forty atmospheres. The volumes of the air and of the carbonic acid were carefully read by a cathetometer, and the results could be relied on with certainty to less than 0·05 millim. The temperature of the water around the carbonic acid tube was ascertained by a thermometer carefully graduated by myself according to an arbitrary scale. This thermometer was one of a set of four, which I constructed some years ago, and which all agreed so closely in their indications, that the differences were found to be altogether insignificant when their readings were reduced to degrees.

I have not attempted to deduce the actual pressure from the observed changes in the volume of the air in the air-tube. For this purpose it would be necessary to know with precision the deviations from the law of Mariotte exhibited by atmospheric air within the range of pressure employed in these experiments, and also the change of capacity in the capillary tube from internal pressure. In a future communication I hope to have an opportunity of considering this problem, which must be resolved rather by indirect than by direct experiments. As regards the deviation of air from Mariotte's law, it corresponds, according to the experiments of Regnault, to an apparent error of a little more than one-fourth of an atmosphere at a pressure of twenty atmospheres, and according to those of Natterer, to an approximate error of one atmosphere when the pressure attains 107 atmospheres. These data are manifestly insufficient, and I have therefore not attempted to deduce the true pressure from the observed change of volume in the air-tube.

It will be easy to apply hereafter the corrections for true pressure when they are ascertained, and for the purposes of this paper they are not required. The general form of the curves representing the changes of volume in carbonic acid will hardly undergo any sensible change from the irregularities in the air-tube; nor will any of the general conclusions at which I have arrived be affected by them. It must, however, always be understood that, when the pressures are occasionally spoken of, as indicated by the apparent contraction of the air in the air-gauge, the approximate pressures only are meant.

To obtain the capacity in cubic centimetres from the weight in grammes of the mercury which filled any part of a glass tube, the following formula was used:—

$$C = W \cdot \frac{1 + 0{\cdot}000154 \cdot t}{13{\cdot}596} \cdot 1{\cdot}00012,$$

where C is the capacity in cubic centims., W the weight of the mercury which filled the tube at the temperature t, 0·000154 the coefficient of apparent expansion of mercury in glass, 13·596 the density of mercury at 0°, and 1·00012 the density of water at 4°.

The volume of the gas V, at 0° and 760 millims. of pressure, was deduced from the double observations, as follows:—

$$V = C \cdot \frac{1}{1 + \alpha t} \cdot \frac{h - d}{760},$$

where C is the capacity of the tube (Figure, page 76) from a to d, or from a to e, t the temperature, α the coefficient of expansion of the gas for heat (0·00366 in the case of air, 0·0037 in that of carbonic acid), h the height of the barometer reduced to 0° and to the latitude of 45°, d the difference of the mercurial columns in the U-tube similarly reduced.

Having thus ascertained the volumes of the air and of the carbonic acid before compression, at 0° and 760 millims., it was easy to calculate their volumes, under the same pressure of 760 millims., at the temperatures at which the measurements were made when the gases were compressed, and thence to deduce the values of the fractions representing the diminution of volume. But the fractions thus obtained would not give results directly comparable for air and carbonic acid. Although the capillary glass tubes in the apparatus (Fig. 6) communicated with the

same reservoir, the pressure on the contained gases was not quite equal, in consequence of the mercurial columns, which confined the air and carbonic acid, being of different heights. The column always stood higher in the carbonic acid tube than in the air-tube, so that the pressure in the latter was a little greater than in the former. The difference in the lengths of the mercurial columns rarely exceeded 200 millims., or about one-fourth of an atmosphere. This correction was always applied, as was also a trifling correction of 7 millims., for a difference of capillary depression in the two tubes.

In order to show more clearly the methods of reduction, I will give the details of one experiment.

Volume of air at 0° and 760 millims. calculated from the observations when the air was expanded to *a e*, 0·3124 cub. centim.

Volume of same air calculated from the observations when the air was expanded to *a d*, 0·3122 cub. centim.

Mean volume of air at 0° and 760 millims., 0·3123 cub. centim.

The volumes of the carbonic acid, deduced in like manner from two independent observations, were 0·3096 cub. centim. and 0·3094 cub. centim. Mean 0·3095 cub. centim.

The length of the column of air after compression, at 10°·76, in the capillary air-tube was 272·9 millims., corresponding to 0·006757 cub. centim. Hence we have

$$\delta' = \frac{0{\cdot}006757}{0{\cdot}3123 \times 1{\cdot}0394} = \frac{1}{48{\cdot}04}.$$

But as the difference in the heights of the mercurial columns in the air-tube and carbonic acid tube, after allowing for the difference of capillary depression, was 178 millims., this result requires a further correction ($\frac{178}{760}$ of an atmosphere), in order to render it comparable with the compression in the carbonic acid tube. The final value for δ, the fraction representing the ratio of the volume of the compressed air at the temperature of the experiment to its volume at the same temperature and under the pressure of one atmosphere, will be

$$\delta = \frac{1}{47{\cdot}81}.$$

The corresponding length of the carbonic acid at 13°·22, in its

capillary tube, was 124·6 millims., equivalent to 0·004211 cub. centim., from which we deduce for the corresponding fraction for the carbonic acid

$$\epsilon = \frac{0{\cdot}004211}{0{\cdot}3095 \times 1{\cdot}0489} = \frac{1}{77{\cdot}09}.$$

Hence it follows that the same pressure, which reduced a given volume of air at 10°·76 to $\frac{1}{47{\cdot}81}$ of its volume at the same temperature under one atmosphere, reduced carbonic acid at 13°·22 to $\frac{1}{77{\cdot}09}$ of its volume at the temperature of 13°·22, and under a pressure of one atmosphere. Or assuming the compression of the air to be approximately a measure of the pressure, we may state that under a pressure of about 47·8 atmospheres carbonic acid at 13°·22 contracts to $\frac{1}{77{\cdot}09}$ of its volume under one atmosphere.

In the following Tables, δ is the fraction representing the ratio of the volumes of the air, after and before compression, to one another, ϵ the corresponding fraction for the carbonic acid, t and t' the temperatures of the air and carbonic acid respectively, l the number of volumes which 17,000 volumes of carbonic acid, measured at 0° and 760 millims., would occupy at the temperature at which the observation was made under the pressure indicated by the air in the air-tube. The values of l are the ordinates of the curve lines shown in the Figure, page 85*.

* As l is the entire volume to which the carbonic acid is reduced, it does not always refer to homogeneous matter, but sometimes to a mixture of gas and liquid. Its value in the example given in the text is obtained as follows:—

$$l = 17000 \cdot \frac{0{\cdot}004211}{0{\cdot}3095} = 231{\cdot}3.$$

When l is homogeneous, $\frac{1}{\epsilon}$ represents the density of the carbonic acid referred to carbonic acid gas, at the temperature t', and under a pressure of one atmosphere.

TABLE I.—*Carbonic Acid at* 13°·1.

δ.	t.	ϵ.	t'.	l.
$\frac{1}{47·50}$	10°·75	$\frac{1}{76·16}$	13°·18	234·1
$\frac{1}{48·76}$	10·86	$\frac{1}{80·43}$	13·18	221·7
$\frac{1}{48·89}$	10·86	$\frac{1}{80·90}$	13·09	220·3
$\frac{1}{49·00}$	10·86	$\frac{1}{105·9}$	13·09	168·2
$\frac{1}{49·08}$	10·86	$\frac{1}{142·0}$	13·09	125·5
$\frac{1}{49·15}$	10·86	$\frac{1}{192·3}$	13·09	92·7
$\frac{1}{49·28}$	10·86	$\frac{1}{268·8}$	13·09	66·3
$\frac{1}{49·45}$	10·86	$\frac{1}{342·8}$	13·09	52·0
$\frac{1}{49·63}$	10·86	$\frac{1}{384·9}$	13·09	46·3
$\frac{1}{50·15}$	10·86	$\frac{1}{462·9}$	13·09	38·5
$\frac{1}{50·38}$	10·86	$\frac{1}{471·5}$	13·09	37·8
$\frac{1}{54·56}$	10·86	$\frac{1}{480·4}$	13·09	37·1
$\frac{1}{75·61}$	10·86	$\frac{1}{500·7}$	13·09	35·6
$\frac{1}{90·43}$	10·86	$\frac{1}{510·7}$	13·09	34·9

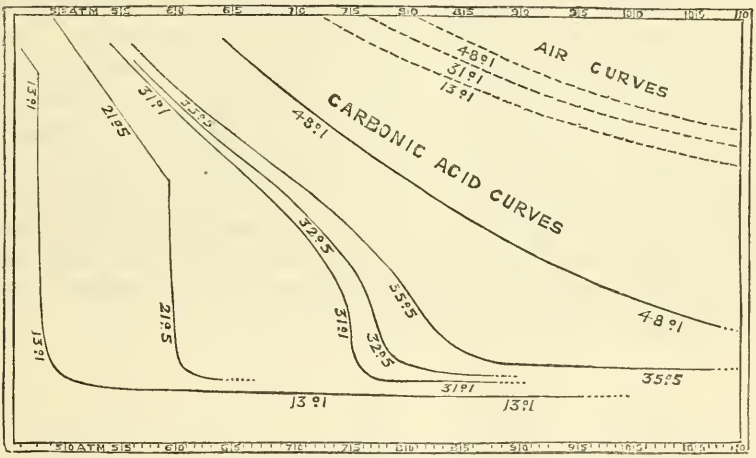
It will be observed that at the pressure of 48·89 atmospheres, as measured by the contraction of the air in the air-tube, liquefaction began. This point could not be fixed by direct observation, inasmuch as the smallest visible quantity of liquid represented a column of gas at least 2 or 3 millims. in length. It was, however, determined indirectly by observing the volume of the gas 0°·2 or 0°·3 above the point of liquefaction, and calculating the contraction the gas would sustain in cooling down to the temperature at which liquefaction began. A slight increase of pressure, it will be seen, was required even in the early stages to carry on the process. Thus the air-gauge, after all reductions were made, indicated an increase of pressure of about one-fourth of an atmosphere (from 48·89 to 49·15 atmospheres) during the condensation of the first and second thirds

of the carbonic acid. According to theory no change of volume ought to have occurred. This apparent anomaly is explained by the presence of the trace of air (about $\frac{1}{500}$ part) in the carbonic acid to which I before referred. It is easy to see that the increase of pressure shown in these experiments is explained by the presence of this small quantity of air. If a given volume of carbonic acid contain $\frac{1}{500}$ of air, that air will be diffused through a space 500 times greater than if the same quantity of air were in a separate state. Compress the mixture till 50 atmospheres of pressure have been applied, and the air will now occupy, or be diffused through, ten times the space it would occupy if alone and under the pressure of one atmosphere; or it will be diffused through the space it would occupy, if alone and under the pressure of $\frac{1}{10}$ of an atmosphere. While the carbonic acid is liquefying, pressure must be applied in order to condense this air; and to reduce it to one-half its volume, an increase of $\frac{1}{10}$ of an atmosphere is required. The actual results obtained by experiment approximate to this calculation. From similar considerations, it follows that if a mixture of air and carbonic acid be taken, for example in equal volumes, the pressure, after liquefaction has begun, must be augmented by several atmospheres, in order to liquefy the whole of the carbonic acid. Direct experiments have shown this conclusion to be true.

The small quantity of air in the carbonic acid disturbed the liquefaction in a marked manner, when nearly the whole of the carbonic acid was liquefied, and when its volume relatively to that of the uncondensed carbonic acid was considerable. It resisted for some time absorption by the liquid, but on raising the pressure to 50·4 atmospheres it was entirely absorbed. If the carbonic acid had been absolutely pure, the part of the curve for 13°·1 (Figure, page 85) representing the fall from the gaseous to the liquid state, would doubtless have been straight throughout its entire course, and parallel to the lines of equal pressure.

TABLE II.—*Carbonic Acid at* 21°·5.

δ.	t.	ϵ.	t'.	l.
$\frac{1}{46{\cdot}70}$	8°·63	$\frac{1}{67{\cdot}26}$	21°·46	272·9
$\frac{1}{60{\cdot}05}$	8·70	$\frac{1}{114{\cdot}7}$	21·46	160·0
$\frac{1}{60{\cdot}29}$	8·70	$\frac{1}{174{\cdot}8}$	21·46	105·0
$\frac{1}{60{\cdot}55}$	8·70	$\frac{1}{240{\cdot}5}$	21·46	76·3
$\frac{1}{61{\cdot}00}$	8·70	$\frac{1}{307{\cdot}7}$	21·46	49·9
$\frac{1}{62{\cdot}21}$	8·70	$\frac{1}{440{\cdot}0}$	21·46	41·7
$\frac{1}{62{\cdot}50}$	8·70	$\frac{1}{443{\cdot}3}$	21·46	41·4



The curve representing the results at 21°·5 agrees in general form with that for 13°·1, as shown in the above figure. At 13°·1, under a pressure of about 49 atmospheres, the volume of carbonic acid is little more than three-fifths of that which a perfect gas would occupy under the same conditions. After liquefaction carbonic acid yields to pressure much more than ordinary liquids; and the compressibility appears to diminish as the pressure increases. The high rate of expansion by heat

of liquid carbonic acid, first noticed by Thilorier, is fully confirmed by this investigation.

The next series of experiments was made at the temperature of 31°·1, or 0°·2 above the point at which, by compression alone, carbonic acid is capable of assuming visibly the liquid form. Since I first announced this fact in 1863, I have made careful experiments to fix precisely the temperature of this critical point in the case of carbonic acid. It was found in three trials to be 30°·92 C., or 87°·7 F. Although for a few degrees above this temperature a rapid fall takes place from increase of pressure, when the gas is reduced to the volume at which it might be expected to liquefy, no separation of the carbonic acid into two distinct conditions of matter occurs, so far as any indication of such a separation is afforded by the action of light. By varying the pressure or temperature, but always keeping the latter above 30°·92, the great changes of density which occur about this point produce the flickering movements I formerly described, resembling in an exaggerated form the appearances exhibited during the mixture of liquids of different densities, or when columns of heated air ascend through colder strata. It is easy so to adjust the pressure that one-half of the tube shall be filled with uncondensed gas and one-half with the condensed liquid. Below the critical temperature this distinction is easily seen to have taken place, from the visible surface of demarcation between the liquid and gas, and from the shifting at the same surface of the image of any perpendicular line placed behind the tube. But above 30°·92 no such appearances are seen, and the most careful examination fails to discover any heterogeneity in the carbonic acid, as it exists in the tube.

TABLE III.—*Carbonic Acid at* 31°·1.

δ.	t.	ϵ.	t'.	l.
$\frac{1}{54{\cdot}79}$	11°·59	$\frac{1}{80{\cdot}55}$	31°·17	235·4
$\frac{1}{55{\cdot}96}$	11·59	$\frac{1}{83{\cdot}39}$	31·22	227·4
$\frac{1}{57{\cdot}18}$	11·58	$\frac{1}{86{\cdot}58}$	31·15	219·0
$\frac{1}{58{\cdot}46}$	11·55	$\frac{1}{90{\cdot}04}$	31·19	210·6
$\frac{1}{59{\cdot}77}$	11·41	$\frac{1}{93{\cdot}86}$	31·18	202·0
$\frac{1}{61{\cdot}18}$	11·40	$\frac{1}{98{\cdot}07}$	31·20	193·3
$\frac{1}{62{\cdot}67}$	11·44	$\frac{1}{103{\cdot}1}$	31·19	183·9
$\frac{1}{64{\cdot}27}$	11·76	$\frac{1}{109{\cdot}6}$	31·13	173·0
$\frac{1}{65{\cdot}90}$	11·73	$\frac{1}{116{\cdot}2}$	31·19	163·2
$\frac{1}{67{\cdot}60}$	11·63	$\frac{1}{124{\cdot}4}$	31·15	152·4
$\frac{1}{69{\cdot}39}$	11·55	$\frac{1}{134{\cdot}5}$	31·03	140·9
$\frac{1}{71{\cdot}25}$	11·40	$\frac{1}{147{\cdot}8}$	31·06	128·2
$\frac{1}{73{\cdot}26}$	11·45	$\frac{1}{169{\cdot}0}$	31·09	112·2
$\frac{1}{73{\cdot}83}$	13·00	$\frac{1}{174{\cdot}4}$	31·08	108·7
$\frac{1}{75{\cdot}40}$	11·62	$\frac{1}{311{\cdot}1}$	31·06	60·9
$\frac{1}{77{\cdot}64}$	11·65	$\frac{1}{369{\cdot}1}$	31·06	51·3
$\frac{1}{79{\cdot}92}$	11·16	$\frac{1}{388{\cdot}0}$	31·10	49·4
$\frac{1}{82{\cdot}44}$	11·23	$\frac{1}{395{\cdot}7}$	31·07	47·9
$\frac{1}{85{\cdot}19}$	11·45	$\frac{1}{405{\cdot}5}$	31·05	46·7

The graphical representation of these experiments, as shown on page 85, exhibits some marked differences from the curves for lower temperatures. The dotted lines in the figure represent a portion of the curves of a perfect gas (assumed to have the same volume at 0° and under one atmosphere as the carbonic acid) for the temperatures of 13°·1, 31°·1, and

48°·1. The volume of the carbonic acid at 31°·1, it will be observed, diminishes with tolerable regularity, but much faster than according to the law of Mariotte, till a pressure of about 73 atmospheres is attained. The diminution of volume then goes on very rapidly, a reduction to nearly one-half taking place, when the pressure is increased from 73 to 75 atmospheres, or only by $\frac{1}{37}$ of the whole pressure. The fall is not, however, abrupt, as in the case of the formation of the liquid at lower temperatures, but a steady increase of pressure is required to carry it through. During this fall, as has already been stated, there is no indication, at any stage of the process, of two conditions of matter being present in the tube. Beyond 77 atmospheres, carbonic acid at 31°·1 yielded much less than before to pressure, its volume having become reduced nearly to that which it ought to occupy as a liquid, at the temperature at which the observations were made.

TABLE IV.—*Carbonic Acid at* 32°·5

δ.	t.	ϵ.	t'.	l.
$\frac{1}{57·38}$	12°·10	$\frac{1}{85·90}$	32°·50	221·7
$\frac{1}{71·52}$	12·15	$\frac{1}{140·3}$	32·34	135·6
$\frac{1}{73·60}$	12·30	$\frac{1}{156·0}$	32·45	122·0
$\frac{1}{74·02}$	12·30	$\frac{1}{159·9}$	32·46	119·1
$\frac{1}{76·25}$	12·40	$\frac{1}{191·7}$	32·38	99·3
$\frac{1}{78·52}$	12·50	$\frac{1}{311·8}$	32·48	61·1
$\frac{1}{79·77}$	12·35	$\frac{1}{351·3}$	32·54	54·2
$\frac{1}{84·90}$	12·35	$\frac{1}{387·8}$	32·75	49·1

TABLE V.—*Carbonic Acid at* 35°·5.

δ.	t.	ϵ.	t'.	l.
$\frac{1}{56\cdot80}$	15°·68	$\frac{1}{82\cdot72}$	35°·49	232·5
$\frac{1}{59\cdot34}$	15·70	$\frac{1}{88\cdot94}$	35·54	216·2
$\frac{1}{62\cdot15}$	15·66	$\frac{1}{96\cdot41}$	35·52	199·5
$\frac{1}{65\cdot23}$	15·66	$\frac{1}{106\cdot0}$	35·51	181·4
$\frac{1}{68\cdot66}$	15·75	$\frac{1}{118\cdot4}$	35·47	162·4
$\frac{1}{72\cdot45}$	15·79	$\frac{1}{135\cdot1}$	35·48	142·3
$\frac{1}{76\cdot58}$	15·52	$\frac{1}{161\cdot2}$	35·55	119·3
$\frac{1}{81\cdot28}$	15·61	$\frac{1}{228\cdot0}$	35·55	84·4
$\frac{1}{86\cdot60}$	15·67	$\frac{1}{351\cdot9}$	35·48	54·6
$\frac{1}{89\cdot52}$	15·67	$\frac{1}{373\cdot7}$	35·50	51·5
$\frac{1}{92\cdot64}$	15·64	$\frac{1}{387\cdot9}$	35·61	49·6
$\frac{1}{99\cdot57}$	15·61	$\frac{1}{411\cdot0}$	35·55	46·8
$\frac{1}{107\cdot6}$	15·47	$\frac{1}{430\cdot2}$	35·53	44·7

TABLE VI.—*Carbonic Acid at* 48°·1.

δ.	t.	ϵ.	t'.	l.
$\frac{1}{62\cdot60}$	15°·67	$\frac{1}{86\cdot45}$	47°·95	231·5
$\frac{1}{68\cdot46}$	15·79	$\frac{1}{99\cdot39}$	48·05	201·4
$\frac{1}{75\cdot58}$	15·87	$\frac{1}{117\cdot8}$	48·12	170·0
$\frac{1}{84\cdot35}$	15·91	$\frac{1}{146\cdot8}$	48·25	136·5
$\frac{1}{95\cdot19}$	15·83	$\frac{1}{198\cdot5}$	48·13	100·8
$\frac{1}{109\cdot4}$	16·23	$\frac{1}{298\cdot4}$	48·25	67·2

The curve for 32°·5 (page 85), resembles closely that for 31°·1. The fall is, however, less abrupt than at the latter temperature. The range of pressure in the experiments at 35°·5 extends from 57 to above 107 atmospheres. The fall is here greatly diminished, and it has nearly lost its abrupt character. It is most considerable from 76 to 87 atmospheres, where an increase of one-seventh in the pressure produces a reduction of volume to one-half. At 107 atmospheres the volume of the carbonic acid has come almost into conformity with that which it should occupy, if it were derived directly from liquid carbonic acid, according to the law of the expansion of that body for heat.

The curve for 48°·1 is very interesting. The fall shown in the curves for lower temperatures has almost, if not altogether, disappeared, and the curve itself approximates to that which would represent the change of volume in a perfect gas. At the same time the contraction is much greater than it would have been if the law of Mariotte had held good at this temperature. Under a pressure of 109 atmospheres, the carbonic acid is rapidly approaching to the volume it would occupy if derived from the expansion of the liquid; and if the experiment had not been interrupted by the bursting of one of the tubes, it would doubtless have fallen into position at a pressure of 120 or 130 atmospheres.

I have not made any measurements at higher temperatures than 48°·1; but it is clear that, as the temperature rises, the curve would continue to approach to that representing the change of volume of a perfect gas.

I have frequently exposed carbonic acid, without making precise measurements, to much higher pressures than any marked in the Tables, and have made it pass, without break or interruption from what is regarded by every one as the gaseous state, to what is, in like manner, universally regarded as the liquid state. Take, for example, a given volume of carbonic acid gas at 50° C., or at a higher temperature, and expose it to increasing pressure till 150 atmospheres have been reached. In this process its volume will steadily diminish as the pressure augments, and no sudden diminution of volume, without the application of external pressure, will occur at any stage of it. When the full pressure has been applied, let the temperature be allowed to fall till the carbonic acid has reached the ordinary tem-

perature of the atmosphere. During the whole of this operation no breach of continuity has occurred. It begins with a gas, and by a series of gradual changes, presenting nowhere any abrupt alteration of volume or sudden evolution of heat, it ends with a liquid. The closest observation fails to discover anywhere indications of a change of condition in the carbonic acid, or evidence, at any period of the process, of part of it being in one physical state and part in another. That the gas has actually changed into a liquid would, indeed, never have been suspected, had it not shown itself to be so changed by entering into ebullition on the removal of the pressure. For convenience, this process has been divided into two stages, the compression of the carbonic acid and its subsequent cooling; but these operations might have been performed simultaneously, if care were taken so to arrange the application of the pressure and the rate of cooling, that the pressure should not be less than 76 atmospheres when the carbonic acid had cooled to 31°.

We are now prepared for the consideration of the following important question. What is the condition of carbonic acid when it passes, at temperatures above 31°, from the gaseous state down to the volume of the liquid, without giving evidence at any part of the process of liquefaction having occurred? Does it continue in the gaseous state, or does it liquefy, or have we to deal with a new condition of matter? If the experiment were made at 100°, or at a higher temperature, when all indications of a fall had disappeared, the probable answer which would be given to this question is that the gas preserves it gaseous condition during the compression; and few would hesitate to declare this statement to be true, if the pressure, as in Natterer's experiments, were applied to such gases as hydrogen or nitrogen. On the other hand, when the experiment is made with carbonic acid at temperatures a little above 31°, the great fall which occurs at one period of the process would lead to the conjecture that liquefaction had actually taken place, although optical tests carefully applied failed at any time to discover the presence of a liquid in contact with a gas. But against this view it may be urged with great force, that the fact of additional pressure being always required for a further diminution of volume, is opposed to the known laws which hold in the change of bodies from the gaseous to the liquid state. Besides, the higher the temperature at which

the gas is compressed, the less the fall becomes, and at last it disappears.

The answer to the foregoing question, according to what appears to me to be the true interpretation of the experiments already described, is to be found in the close and intimate relations which subsist between the gaseous and liquid states of matter. The ordinary gaseous and ordinary liquid states are, in short, only widely separated forms of the same condition of matter, and may be made to pass into one another by a series of gradations so gentle that the passage shall nowhere present any interruption or breach of continuity. From carbonic acid as a perfect gas to carbonic acid as a perfect liquid, the transition we have seen may be accomplished by a continuous process, and the gas and liquid are only distant stages of a long series of continuous physical changes. Under certain conditions of temperature and pressure, carbonic acid finds itself, it is true, in what may be described as a state of instability, and suddenly passes, with evolution of heat, and without application of additional pressure or change of temperature, to the volume, which by the continuous process can only be reached through a long and circuitous route. In the abrupt change which here occurs, a marked difference is exhibited, while the process is going on, in the optical and other physical properties of the carbonic acid which has collapsed into the smaller volume, and of the carbonic acid not yet altered. There is no difficulty here, therefore, in distinguishing between the liquid and the gas. But in other cases the distinction cannot be made; and under many of the conditions I have described it would be vain to attempt to assign carbonic acid to the liquid rather than the gaseous state. Carbonic acid, at the temperature of 35°·5, and under a pressure of 108 atmospheres, is reduced to $\frac{1}{130}$ of the volume it occupied under a pressure of one atmosphere; but if any one ask whether it is now in the gaseous or liquid state, the question does not, I believe, admit of a positive reply. Carbonic acid at 35°·5, and under 108 atmospheres of pressure, stands nearly midway between the gas and the liquid; and we have no valid grounds for assigning it to the one form of matter any more than to the other. The same observation would apply with even greater force to the state in which carbonic acid exists at higher temperatures and under greater pressures than those just mentioned.

In the original experiment of Cagniard de la Tour, that distinguished physicist inferred that the liquid had disappeared, and had changed into a gas. A slight modification of the conditions of his experiment would have led him to the opposite conclusion, that what had been before a gas was changed into a liquid. These conditions are, in short, the intermediate states which matter assumes in passing, without sudden change of volume, or abrupt evolution of heat, from the ordinary liquid to the ordinary gaseous state.

In the foregoing observations I have avoided all reference to the molecular forces brought into play in these experiments. The resistance of liquids and gases to external pressure tending to produce a diminution of volume, proves the existence of an internal force of an expansive or resisting character. On the other hand, the sudden diminution of volume, without the application of additional pressure externally, which occurs when a gas is compressed, at any temperature below the critical point, to the volume at which liquefaction begins, can scarcely be explained without assuming that a molecular force of great attractive power comes here into operation, and overcomes the resistance to diminution of volume, which commonly requires the application of external force. When the passage from the gaseous to the liquid state is effected by the continuous process described in the foregoing pages, these molecular forces are so modified as to be unable at any stage of the process to overcome alone the resistance of the fluid to change of volume.

The properties described in this communication, as exhibited by carbonic acid, are not peculiar to it, but are generally true of all bodies which can be obtained as gases and liquids. Nitrous oxide, hydrochloric acid, ammonia, sulphuric ether, and sulphuret of carbon, all exhibited, at fixed pressures and temperatures, critical points, and rapid changes of volume with flickering movements, when the temperature or pressure was changed in the neighbourhood of those points. The critical points of some of these bodies were above 100°; and in order to make the observations, it was necessary to bend the capillary tube before the commencement of the experiment, and to heat it in a bath of paraffin or oil of vitriol.

The distinction between a gas and vapour has hitherto been founded on principles which are altogether arbitrary. Ether in the state of gas is called a vapour, while sulphurous acid in

the same state is called a gas; yet they are both vapours, the one derived from a liquid boiling at 35°, the other from a liquid boiling at − 10°. The distinction is thus determined by the trivial condition of the boiling point of the liquid, under the pressure of the atmosphere, being higher or lower than the ordinary temperature of the atmosphere. Such a distinction may have some advantages for practical reference, but it has no scientific value. The critical point of temperature affords a criterion for distinguishing a vapour from a gas, if it be considered important to maintain the distinction at all. Many of the properties of vapours depend on the gas and liquid being present in contact with one another; and this, we have seen, can only occur at temperatures below the critical point. We may accordingly define a vapour to be a gas at any temperature under its critical point. According to this definition, a vapour may, by pressure alone, be changed into a liquid, and may therefore exist in presence of its own liquid; while a gas cannot be liquefied by pressure, that is, so changed by pressure as to become a visible liquid distinguished by a surface of demarcation from the gas. If this definition be accepted, carbonic acid will be a vapour below 31°, a gas above that temperature; ether, a vapour below 200°, a gas above that temperature.

We have seen that the gaseous and liquid states are only distant stages of the same condition of matter, and are capable of passing into one another by a process of continuous change. A problem of far greater difficulty yet remains to be solved, the possible continuity of the liquid and solid states of matter. The fine discovery made some years ago by James Thomson, of the influence of pressure on the temperature at which liquefaction occurs, and verified experimentally by Sir W. Thomson, points, as it appears to me, to the direction this inquiry must take; and in the case at least of those bodies which expand in liquefying, and whose melting points are raised by pressure, the transition may possibly be effected. But this must be a subject for future investigation; and for the present I will not venture to go beyond the conclusion I have already drawn from direct experiment, that the gaseous and liquid forms of matter may be transformed into one another by a series of continuous and unbroken changes.

Appendix.

The following experiments, made at temperatures differing from any of the foregoing series, are added, as they may hereafter be useful for reference.

δ.	t.	ϵ.	t'.
$\frac{1}{48\cdot15}$	12°·42	$\frac{1}{75\cdot00}$	15°·76
$\frac{1}{53\cdot04}$	11·13	$\frac{1}{92\cdot53}$	16·45
$\frac{1}{47\cdot45}$	11·50	$\frac{1}{64\cdot14}$	31·91
$\frac{1}{71\cdot75}$	13·10	$\frac{1}{148\cdot5}$	31·65
$\frac{1}{73\cdot88}$	13·20	$\frac{1}{170\cdot5}$	31·71
$\frac{1}{73\cdot92}$	13·20	$\frac{1}{157\cdot9}$	33·15
$\frac{1}{73\cdot77}$	12·74	$\frac{1}{152\cdot3}$	33·58
$\frac{1}{73\cdot89}$	13·14	$\frac{1}{144\cdot5}$	35·00
$\frac{1}{73\cdot89}$	13·21	$\frac{1}{140\cdot0}$	36·03
$\frac{1}{76\cdot05}$	13·27	$\frac{1}{153\cdot4}$	36·05
$\frac{1}{78\cdot35}$	13·38	$\frac{1}{171\cdot1}$	36·11
$\frac{1}{80\cdot74}$	13·40	$\frac{1}{197\cdot8}$	36·22
$\frac{1}{83\cdot31}$	13·45	$\frac{1}{251\cdot4}$	36·20
$\frac{1}{86\cdot01}$	13·50	$\frac{1}{323\cdot6}$	36·08
$\frac{1}{88\cdot92}$	13·53	$\frac{1}{358\cdot1}$	36·18
$\frac{1}{92\cdot06}$	13·55	$\frac{1}{377\cdot8}$	36·22

XII.—*Note on some Reactions of Alcohols.*

By Ernest Theophron Chapman.

(Read February 3rd, 1870.)

Amylic Alcohol.—This alcohol, as commonly obtained, is found to rotate a ray of polarized light to a greater or less extent. In fact, it consists of two alcohols, the one rotating and the other non-rotating. These two alcohols may be separated, though only with great labour, by re-crystallising their sulph-amylates of baryta. They may also be separated, to a great extent, and one (the non-rotating) may be obtained quite pure by distilling the mixed alcohol from soda, chloride of calcium, acetate of potash, and many other substances which are soluble in the alcohol. The non-rotating alcohol is always retained and the rotating alcohol distils over. But unfortunately the case is not quite so simple as it appears; for I find that the rotating alcohol may be converted into the non-rotating alcohol by the very treatment employed to separate it from the non-rotating. I first became aware of this by finding that, though the rotation of a fraction of a sample of amylic alcohol could be increased by distilling it with soda, still on mixing the fraction retained by the soda with that which distilled over, the rotation was always found to be less than that of the sample before it had been submitted to treatment. I do not think that either acetate of potash or chloride of calcium has the property of lowering the rotating power, but they do not separate the two alcohols so fast as soda does. Absolutely non-rotating amylic alcohol may be obtained in any quantity by distilling a solution of caustic soda in amylic alcohol to dryness. On adding water to the dry mass in the retort and distilling, we get an almost non-rotating alcohol which, by another similar treatment, may be made quite non-rotating. I cannot find that this non-rotating alcohol presents any differences from the common mixed rotating and non-rotating alcohol in other physical properties.

The compounds of the non-rotating alcohol do not rotate, those of the rotating alcohol do. This remark applies to the iodide, bromide, chloride, nitrate, and nitrite. The compounds rotate in the opposite direction to the alcohol. The valerianic

acid, as is well known, also rotates in the opposite direction from the alcohol from which it is obtained.

It would appear that the internal structure of organic compounds is not so permanent as we have been in the habit of thinking. We must, therefore, most carefully avoid the use of powerful reagents whenever we wish to examine a question of internal structure.

In our paper on Butylic Alcohol (Jour. Chem. Soc., March, 1869), Mr. Miles H. Smith and I state that "butylic alcohol cannot be dried by treatment with sodium. It would appear that hydrated oxide of sodium is more or less decomposed by butylic alcohol, water and butylate of sodium being the products." This supposition appears to be quite correct, as the following experiments on amylic alcohol tend to prove.

About 400 grms. of dry amylic alcohol were placed in a weighed flask along with 9 grms. water. About 11½ grms. of sodium was now added, a small portion at a time. The contents of the flask were now distilled in the oil-bath to dryness, the temperature being allowed to rise to 230 C., at which it was maintained for about two hours. On weighing, it was found that the residue weighed 58 grms. In the distillation, much water came over at first. The residue in the retort was very light and porous. On adding water to the contents of the retort, and distilling, amylic alcohol came over, accompanied by water. On adding carbonate of potash and separating the amylic alcohol, drying and weighing it, it was found to weigh 46 grms. As the alcohol gained hydrogen from the water added (½ grm.), we find that the residue must have consisted for the most part of amylate of soda, with only a small portion of caustic soda. Had it consisted of caustic soda retaining amylic alcohol, we should only have obtained 38 instead of 45 grms. of the alcohol from it. We thus see that the sodium replaces the hydrogen in the amylic alcohol under the conditions of this experiment rather than the hydrogen in the water.

I now took 20 grms. of pure, freshly-fused caustic soda and dissolved it in about 500 grms. of amylic alcohol. A clear solution was obtained. It was distilled, as in the last case, with exactly the same result, nearly the whole of the soda being converted into the amylate. In this case the amylic alcohol vapour which remained in the retort after the experi-

ment was expelled by a stream of hydrogen. The weight of the amylate of soda was about 56½ grms. Theoretically, it should have yielded 55 grms. From these 56½ grms. 46 grms. of amylic alcohol were obtained. In this case also water was observed to distil out with the amylic alcohol. Here, then, we see that the sodium in the caustic soda actually changes place with the hydrogen of the amylic alcohol.

XIII.—*Note on the Organic Matter contained in Air.*

By Ernest Theophron Chapman.

(Read February 3rd, 1870.)

The following slight investigation on the organic matters contained in air is published in its present very incomplete state, because I do not see any chance of being able to do much more to it for a long time to come.

When Mr. Wanklyn, Mr. M. H. Smith, and myself first became aware that we could detect, and in a measure estimate, the most minute traces of nitrogenous organic matter in water, by converting a part or the whole of the nitrogen it contained into ammonia, and estimating this by the Nessler test, it occurred to us that we might extend the process to air by washing the air with water, and examining the water.

The first experiments on this subject were made by Mr. Wanklyn. He took a large bottle and filled it with the air to be examined, added some pure water, and agitated the bottle. His results were of an indecisive character, I should think, because the volume of air operated upon was too small, and the method of bringing the air and water into contact was not sufficiently complete. So far as I know the matter rested here until I took it in hand. The first and most obvious experiment was to draw air through a Liebig's potash-bulb apparatus charged with water. This was not satisfactory, though when about 100 litres had been passed through the bulbs, the water was found to contain nitrogenous organic matter; but if the air was sent through a second set of bulbs they also were

found to contain nitrogenous organic matter in quantity almost equal to the first. The quantities of nitrogenous organic matter separated from the air in this way were also very small. I next tried a tube with twenty-five bulbs blown on it, so that the air had to bubble through each of the twenty-five; this was better, but still very bad. I then tried cotton-wool as a filter, but found it impossible to get cotton-wool which was itself free from nitrogenous impurities. I then tried gun-cotton, and found that when made with care it did pretty well, but a much thicker plug of it is required than of cotton-wool; it is very liable to contract organic impurities from the air, and if I am not mistaken, it sometimes contains nitrogenous organic matter of a kind which yields ammonia when heated with potash and permanganate of potash. I next tried washing the air by condensing steam in it. This method answered better than any of those described above, but, as will be seen, I found a much simpler method afterwards. I next attempted to wash the air by causing spray to pass through it; this method is about on a par with the last. I then tried a kind of inorganic paper made of asbestos; the asbestos was crushed by pressure between flat surfaces, so as not to break its fibre more than could be helped; it was now ignited and then boiled with dilute potash and permanganate of potash, and the hot liquid with the asbestos suspended in it was poured on to a piece of wire-gauze which had been fastened with plaster of Paris into a funnel. It was now washed with distilled water, and then air drawn through it whilst it was still wet. This filter answers very well, if well made, but it is very troublesome to make.

Lastly I employed pumice-stone, powdered till it became as fine as very fine sand. It was employed just as the asbestos had been, but it only requires to be heated to redness. First a little rather coarse pumice is sprinkled on the wire gauze, then about half an inch of the fine powder, the whole is then damped, and air drawn through it.

This filter possesses all the advantages required: it removes all the suspended matter from the air, and is itself easily rendered free from every suspicion of organic matter. I construct it as follows:—A wide-necked funnel, about four inches in diameter, is fitted into the neck of a Woulfe's bottle; a smaller funnel has its neck removed and is slipped inside the larger one, so that its rim shall be about an inch within the

rim of the other funnel. On the inner rim rests a disc of wire-gauze, on which the powdered pumice is spread; the other neck of the Woulfe's bottle is connected with a large aspirator.

When it is wished to examine air, the apparatus is first thoroughly cleaned, and the pumice is ignited and then boiled with water, it is then placed on the wire-gauze and the air to be examined is drawn through the apparatus; the pumice should be damped from time to time. When sufficient air, say 100 litres, has been passed through the apparatus, the pumice is transferred to a retort which contains water that has been freed from ammonia and organic matter, the water in the Woulfe's bottle is added, and the operation proceeded with exactly as if it were an estimation of nitrogenous organic matter in a sample of water by the "ammonia method." Some little difficulty will be experienced in managing the boiling, and it is for this reason that I prefer pumice to sand.

I have not had either time or opportunity to make many examinations by this method; the general results arrived at are, that the air of crowded rooms contains suspended nitrogenous organic matter, and in addition such air contains volatile organic bases: for when pumice is boiled with carbonate of soda before the addition of permanganate, the distillate is found to contain ammonia and organic bases; this is easily proved by dividing the distillate into two portions, and pouring the one into a retort containing a boiling solution of potash and permanganate of potash. If now the same volume of liquid be distilled over which was added to the permanganate solution it will be found that on adding Nessler test to the portion of the distillate from the pumice which has been treated with permanganate, a very much deeper coloration will be given than that given by the portion which has not been so treated.

This method of proceeding is so simple, and moreover so quick, that we can get a very good idea of the purity of the air in a couple of hours. I regard the presence of the volatile bases as of more importance than the solid organic matter, because this latter may consist of harmless material such as the hurl from woollen cloth, &c.

Air collected from the neighbourhood of an untrapped sink may be shown to contain notable quantities both of volatile organic bases, and of non-volatile organic matter.

I have not hitherto made any experiment the results of which possess any interest, further than that they establish the fact that perceptible quantities of ammonia may be extracted from the organic matter contained in 100 litres of air.

I have found quantities, varying from ·02 milligramme up to ·35 in the air of rooms; the quantity of ammonia is very variable. The quantity of nitrogen existing as volatile organic bases is extremely difficult to determine, but appears generally to run pretty nearly parallel to the amount of ammonia.

It was my intention to have carried out a very complete investigation by means of the method here sketched, on the ventilation of hospitals, fever-wards, and the like; I have not now the opportunity of doing so, and publish this fragment in the hope that some one may be induced to carry out the investigation which I purposed.

XIV.—*Refraction Equivalents.*

By J. H. Gladstone, Ph.D., F.R.S.

[A Lecture delivered before the Chemical Society, March 3rd, 1870.]

There were three distinct lines of research which led up to the discovery of refraction equivalents. The first was the influence of temperature on the refraction of light by liquids; the second, the refraction of mixtures or combinations as compared with that of their constituents; and the third, the refractive indices of different members of homologous series of organic compounds.

As to the first of these, it must have been frequently observed that a liquid bent the rays of light differently when it was heated, but the late Rev. Baden Powell seems to have been the first to investigate the matter, and the Rev. T. Pelham Dale and myself, carrying out his idea, and with his instrument, found that both the refraction and the dispersion always decrease as the temperature rises.* On further examination we

* Phil. Trans., 1858, p. 887.

observed a close relation between the change of density and the change of the refractive index minus unity, which we termed the "refractive energy," and which is expressed in the symbolic language of opticians as $\mu - 1$. The product of this refractive energy with the volume, that is $(\mu - 1)$ vol., or, which is the same thing, the energy divided by the density, that is $\frac{\mu - 1}{d}$; we called the "specific refractive energy," and we came to the conclusion that in the case of liquids this specific refractive energy is a constant not affected by temperature. Nevertheless we recognized "some influence, arising wholly or partially from dispersion, which we have not been able to take into account, but which gives rise to the slight progression of most of the calculated products, and perhaps to the non-inversion of the sensitiveness of water at 4° C., remarked on already by Jamin and ourselves."*

This general conclusion was subsequently confirmed by the experiments of Professor Landolt of Bonn, and a rigorous investigation of the matter by Wüllner† has shown that we were justified in our belief that $\frac{\mu - 1}{d}$, though the best simple formula, does not express the whole truth. The same is exhibited by the very careful determinations of the refraction of water at temperatures ranging from 0° to 100° C., lately published by Kühlmann.‡

The value of this investigation in its bearing on refraction equivalents was, that it drew attention to the specific refractive energy $\frac{\mu - 1}{d}$. Heretofore Newton's "Absolute refractive power," $\frac{\mu_2 - 1}{d}$, had generally engrossed the thoughts of physicists.

As to the second line of research, that of the refraction of mixtures, solutions, and simple combinations, Dulong attempted to show, in regard to gases, and Höck in regard to some liquids, that the absolute refractive power of a mixture is the mean of the absolute refractive powers of its constituents. Mr. Dale and myself, however, on examining the mixtures of substances so widely apart in their refractive power as bisulphide of carbon

* Phil. Trans., 1863, p. 323.

† Pogg Ann., cxxxiii, 1. ‡ Pogg. Ann., cxxxii, 1, 177.

and ether, or aniline and alcohol, came to the conclusion that here also the nearest approximation to the truth was given by adopting $\frac{\mu - 1}{d}$ instead of $\frac{\mu_2 - 1}{d}$. This explains Dulong's observations on gases equally well. This conclusion also has since been fully confirmed by the careful experiments of Wüllner.

To pass from a mixture of two liquids to a solution of a gas or a solid is an easy step, and at the meeting of the British Association in 1863 we showed, among other things, that the same law applied when ammonia gas was dissolved in water, or when solutions were made of sugar or common salt.* The fact that the specific refractive energy of a solid body is not changed by its undergoing solution, was rendered probable in the first place by the fact that water, phosphorus, and sulphur have the same energies in the liquid and solid states;† and it has since been confirmed in other instances, and by the discovery that salts have the same influence on light, whether they be dissolved in water or in alcohol.

At an early stage of our enquiry the question naturally presented itself—does an elementary substance retain its specific power of retarding rays when it is combined chemically with other elements? All our early experiments were made with liquids, and an affirmative reply was suggested by many considerations. One of the most striking I remember was one that is not pointed out in our paper, namely, that bromoform and bibromide of bromethylene, which contain respectively 95 and 90 per cent. of bromine, have almost the same specific refractive energy, and this a remarkably low one, almost identical with that of the liquid halogen itself, though they differ from it so widely in colour, odour, and other physical properties.

Bromoform	$CHBr_3$	·210
Bibromide of bromethylene ..	$C_2H_3Br_3$	·222
Bromine	Br	·212

On the other hand, however, we remarked that isomeric liquids are not always identical in refractive energy, and that

* Brit. Assoc. Report, 1863. Trans., Sec. p. 13.

† Ibid. The details of many of these experiments are given in the Quarterly Journal Chem. Soc., 1865, pp. 110—113.

the substitution of oxygen for hydrogen in organic compounds effects a much greater amount of optical change in some instances than in others. Hence we ventured to draw the conclusion that "every liquid has a specific refractive energy composed of the specific refractive energies of its component elements," but we cautiously added, "modified by the manner of combination."

We subsequently recognized that the combination of hydrochloric acid gas or sulphuric acid with water is sufficient slightly to modify the refractive energy; we knew that Dulong's numbers for the simple and compound gases show that the law of the mean does not hold perfectly true in that region, and trying it on several substances we found that the observed numbers differed, but not very widely, from the calculated mean. One of these substances was ether, which consists of 64·9 per cent. of carbon, 13·5 per cent. of hydrogen, and 21·6 per cent. of oxygen, and taking the specific refractive energy of carbon (Diamond) at ·44, that of hydrogen at 1·533, and oxygen at ·19 (gases determined by Dulong), we obtained—

$$\text{Ether} = \frac{64{\cdot}9\,(\cdot44) + 13{\cdot}5\,(1{\cdot}533) + 21{\cdot}6\,(\cdot19)}{100} = \cdot53$$

Specific refractive energy deduced from observation = ·49

The third line of research was the refraction of different homologous compounds. Professor Delffs (of Heidelberg) first attacked this question in 1853;* Mr. Dale and I made a great many observations,† and Professor Landolt travelled over a similar region at about the same time.‡ From these experiments it was evident that in "all the series containing the compound radicals, methyl and its congeners," the specific refractive energies "increase as the series advances," and that "the amount of optical change is less between the higher than between the lower members of the series."

Landolt subsequently gave the full explanation of this.§ Adopting our $\frac{\mu - 1}{d}$, he multiplied it by the atomic weight, P;

* Pogg., 81, p. 470.
† Phil. Trans., 1863, pp. 325—331.
‡ Pogg., 117, p. 353; 122, p. 545.
§ Pogg., 123, p. 595.

and this $P\frac{\mu-1}{d}$ he designated the "refraction equivalent." Instead of saying with us that the specific refractive energy of a compound is the mean of the specific refractive energies of its constituents, he expressed the same fact thus:—Its refraction equivalent is the sum of the refraction equivalents of its constituent elements. The great advantage of this was that it rendered the calculation more simple, and permitted of the easy comparison of the optical properties of different substances. By making these comparisons, Landolt arrived at the conclusion that the refraction equivalent of carbon is 5·0, that of hydrogen 1·3, and that of oxygen 3·0. Diamond would give 4·85, and Dulong's determination of the gases, respectively, 1·53 and 3·04. The way of calculating the refraction equivalent of a compound from these data may also be illustrated by ether, one of the substances which he likewise examined—

$C_4H_{10}O = 4(5{\cdot}0) + 10(1{\cdot}3) + 3{\cdot}0 \ldots\ldots\ldots = 36{\cdot}0$

Refraction equivalent deduced from observation..... $= 36{\cdot}26$

Landolt showed that the calculated and the experimental refraction equivalents were almost identical for a large number of liquids containing C, H, and O; and he proposed this as a method of quantitative analysis applicable to many mixtures which could not otherwise be easily determined, such as methylic mixed with ethylic alcohol.

From our old observations additional proof was at once derived that carbon might be taken at 5·0, and hydrogen at 1·3, and this being settled it was easy to calculate values for chlorine, bromine, iodine, tin, and mercury. These I communicated to the Chemical Society in a verbal discourse, together with the values of phosphorus, sulphur, nitrogen, and sodium, as deduced from various experiments, but these numbers I regarded as only approximately true.*

There subsequently appeared a valuable paper by Dr. A. Haagen,† in which he examined a variety of liquid haloïd combinations, and deduced from them the refraction equivalents of most of the elements I had determined, together with those of arsenic, antimony, and silicium.

* Chem. News, May 26, 1865. † Pogg., 123, p. 125.

His numbers are:—

Chlorine.....	9·79	Arsenic	20·22
Bromine	15·34	Antimony	25·66
Iodine	24·87	Tin.....	19·89
Phosphorus ..	14·93	Silicium.....	7·90
Sulphur.....	16·03	Sodium	4·89

Ketteler* having taken the refraction of liquid sulphurous acid, found that it was not in accordance with the known refraction of the gas as long as he compared their refractive powers $\frac{\mu_2 - 1}{d}$, but the two came into agreement when he turned to the specific refractive energy, $\frac{\mu - 1}{d}$. The numbers are, gaseous 14·9, liquid 14·6.

Schrauf† has written much upon the subject, and still contends for $\frac{\mu_2 - 1}{d}$.

The following table of compounds of carbon not mentioned in Landolt's or Haagen's papers will show how closely the experimental agree with the calculated numbers, notwithstanding the great diversity of the compounds examined. The equivalents adopted are those which I now prefer, and represent the line A of the solar spectrum:—

C = 5·0	H = 1·3	O = 2·9
Cl = 9·9	Br = 15·3	I = 24·5
S = 16·0	N = 4·1	K = 8·1

The data which have not hitherto been published are given in the appendix.

* Pogg., 124, p. 390. † Pogg., 133, p. 479.

Substance.	Formula.	Condition.	Refraction equivalent.	
			Observed.	Calculated.
Olefiant gas	C_2H_4	Gas..	15.1	15·2
Amylene.	C_5H_{10}	Liquid	37.6	38·0
Hydride of œnanthyl ..	C_7H_{16}	Liquid	55·0	55·8
Hydride of capryl	C_8H_{18}	Liquid	63·0	63·4
Oil of turpentine	$C_{10}H_{16}$	Liquid	72·5	70·8
Oil of patchouli	$C_{15}H_{24}$	Liquid	110·0	106·2
Colophene	$C_{20}H_{32}$	Liquid	147·2	141·6
Hydrate of turpentine ..	$C_{10}H_{16}(H_2O)_3$	Solution in alcohol	89·2	88·6
Camphor	$C_{10}H_{16}O$	Solution in alcohol	73·1	73·7
Peppermint camphor ..	$C_{10}H_{20}O$	Melted	79·0	78·9
Bihydrate of cajeput ..	$C_{10}H_{18}O$	Liquid	76·2	76 3
Wormwood..	$C_{11}H_{16}O$	Liquid	74·5	73·7
Methylated acetone ..	C_4H_8O	Liquid	33·9	33·3
Butyrone	$C_7H_{14}O$	Liquid	56·3	56·1
Laurostearate of ethyl ..	$C_{14}H_{28}O_2$	Liquid	111·5	112·2
Propionate of ethyl ..	$C_5H_{10}O_2$	Liquid	44·2	43·8
Oxalate of ethyl	$C_6H_{10}O_4$	Liquid	51·2	54·6
Oxalate of amyl	$C_{12}H_{22}O_4$	Liquid	99·0	100·2
Carbonate of ethyl.. ..	$C_5H_{10}O_3$	Liquid	45·9	46·7
Caprylic alcohol	$C_8H_{18}O$	Liquid	66·2	66·3
Sugar	$C_{12}H_{22}O_{11}$	Crystallised ..	119·3	120·5
Sugar	$C_{12}H_{22}O_{11}$	Solution in water..	119·2	120·5
Citric acid	$C_6H_8O_7$	Solution in water..	60·9	61·4
Racemic acid	$C_4H_6O_6$	Solution in water..	45·5	45·8
Tartaric acid	$C_4H_6O_6$	Solution in water..	45·3	45·8
Oxalic acid..	$C_2H_2O_4$	Solution in water..	23·4	24·2
Formate of potassium ..	$CKHO_2$	Solution in water..	20·2	20·0
Acetate of potassium ..	$C_2KH_3O_2$	Solution in water..	27·8	27·8
Lactate of potassium ..	$C_6K_2H_{10}O_6$	Solution in water..	76·3	76·6
Succinate of potassium ..	$C_4K_2H_4O_4$	Solution in water..	52·4	53·0
Cyanogen	CN	Gas..	9·2	9·1
Cyanide of ethyl	C_3NH_5	Liquid	25·6	25·6
Cyanide of potassium ..	CNK	Solution in water..	17·2	17·2
Sulphocyanide of potassium	$CNSK$	Solution in water..	33·5	33·2
Urea	CN_2H_4O	Solution in water..	22·8	21·3
Nicotine	$C_{10}N_2H_{14}$	Liquid	74·3	76·4
Chloride of acetyl.. ..	C_2H_3ClO	Liquid	27·0	26·7
Chloropicrin	CNO_2Cl_3	Liquid	45·2	44·6
Chloral	C_2HOCl_3	Liquid	47·5	43 9
Bichloride of chlorethylene	$C_2H_3Cl_3$	Liquid	43 5	43 6
Hydrochlorate of camphene	$C_{10}H_{17}Cl$	Solution in alcohol	82·1	82·0
Bromoform..	$CHBr_3$	Liquid	53·3	52·2
Bibromide of chlorethylene	$C_2H_3Br_2Cl$	Liquid	53·7	54·4
Bibromide of bromethylene	$C_2H_3Br_3$	Liquid	59·3	59·8
Iodide of propyl	C_3H_7I	Liquid	49·0	48·6
Iodoform	CHI_3	Solution in ether..	77·5	79·8
Carbonic oxide	CO	Gas..	7·5	7·9
Carbonic acid	CO_2	Gas..	10·0	10·8
Carbonate of potassium ..	CK_2O_3	Solution in water..	28·8	29·9

Yet there are exceptions to this agreement with theory. The most remarkable is the whole group of the aromatic hydro-

carbons and their derivatives, which give refraction equivalents from 6 to 9 above the calculated numbers. I shall discuss these in a separate communication, and show reasons for thinking that the anomaly must be due to something in the constitution of the nucleus common to the whole group, and which cannot be greater than C_6H_3.

The fact that a substance retains the same specific refractive energy, and consequently the same refraction equivalent, when dissolved, afforded the means of determining the equivalents of a great number of solid bodies, which could not otherwise be taken. The idea occurred to me of examining metallic salts in this way in the hope of arriving at the refraction equivalents of the metals. A series of chlorides, bromides, and iodides, were first tried, the refractive indices of their solution in water being taken, and the due deduction being made for the solvent. The following are specimens of the early results:—

	Chloride.	Bromide.	Iodide.
Potassium	18·83	25·09	35·72
Sodium	15·40	21·89	32·52
Lithium	14·86	20·56	31·49
Ammonium	22·33	28·53	38·90

That a chloride had in each case a refraction equivalent about 6 less than the corresponding bromide, and about 17 less than the corresponding iodide, and that a potassium salt had in each case a refraction equivalent about 3·2 greater than the corresponding sodium salt, about 4 greater than the lithium, and about 3·5 less than the ammonium salt, seemed enough to prove three things:—1st, that the different salts were really comparable with one another in this respect; 2nd, that each halogen and each metal retained its own refractive power with whatever it was combined; 3rd, that if we were certain of the value of any one of these elements, we could determine all the rest.

These experiments have been extended to about 180 different salts, containing 28 inorganic salt-radicals, and 33 metals. Most of these have been tabulated in a paper sent to the Royal Society last July, and now being printed.

A variety of methods were employed for determining the

value of potassium,* and they led to the conclusion that the refraction equivalent of that element in its salts is 8·1, subject to an error probably not exceeding ± 0·1. Starting from this value it was easy to calculate equivalents for every other component of these salts in solution.

By attacking the question from different points, the following refraction equivalents have been determined for elementary substances:—

Element.	Atomic weight.	Refraction equivalent.
Aluminium	27·4	8·4
Antimony	122	24·5
Arsenic	75	15·4 (other values ?)
Barium	137	15·8
Bismuth	210	39·2
Boron	11	4·0
Bromine	80	15·3 In dissolved salts 16·9
Cadmium	112	13·6
Cœsium	133	13·7 ?
Calcium	40	10·4
Carbon	12	5·0
Cerium	92	13·6 ?
Chlorine	35·5	9·9 In dissolved salts 10·7
Chromium	52·2	15·9 In chromates 23 ?
Cobalt	58·8	10·8
Copper	63·4	11·6
Didymium	96	16·0 ?
Fluorine	19	1·4 ?
Glucinum	9·4	5·7
Gold	197	24·0
Hydrogen	1	1·3 In hydracids 3·5
Iodine	127	24·5 In dissolved salts 27·2
Iron	56	12·0 In ferric salts 20·1
Lead	207	24·8
Lithium	7	3·8
Magnesium	24	7·0
Manganese	55	12·2 In permanganate 26·2 ?
Mercury	200	21·3 In compound iodides 29·0
Nickel	58·8	10·4
Nitrogen	14	4·1 In high oxides 5·3
Oxygen	16	2·9
Palladium	106·5	22·2
Phosphorus	31	18·3 (other values ?)
Platinum	197·4	26·0
Potassium	39·1	8·1
Rhodium	104·4	24·2 ?
Rubidium	85·4	14·0
Silicon	28	7·5 ? In silicates 6·8
Silver	108	13·5 (other values ?)
Sodium	23	4·8
Strontium	87·5	13·6

* See Proc. Royal Society, 1868, p. 439, as well as complete paper.

Element.	Atomic weight.	Refraction equivalent.
Sulphur	32	16·0 (other values ?)
Thallium	204	21·6 ?
Tin	118	27·0 In tetrachloride 19·2
Titanium	50	25·5 ?
Uranium	120	10·8
Vanadium	51·2	25·3 ?
Zinc..	65·2	10·2
Zirconium	89·6	22·3 ?

The sign ? in the above table indicates that the equivalent has been deduced from only one compound, or that the different determinations are not fairly accordant. Of the rest, some few are, I believe, as accurate as the atomic weights themselves; but most are open to rectification in the first place of decimals.

It will be seen that many of these elements have a double value. This is a source of difficulty, but the disadvantage is far more than counterbalanced by the promise it holds out of throwing new light on the constitution of bodies. If an element had always the same refraction equivalent in whatever way it might be combined, the determination of the numbers would be very easy, and there might be some curious relations between them, but beyond that they could have little interest for the chemical philosopher. If, on the contrary, every difference in the manner of combination were to affect the rate at which light is propagated by an element, the problem would be very complex, and valuable deductions would be almost hopeless. The fact, however, is intermediate between these; an element usually exerts the same influence on transmitted rays in all analogous compounds, and in many that are not analogous, but there are differences of composition which do affect this quality, and in some cases at least these are coincident with a change of atomicity.

Thus iron in all the ferrous salts examined has the equivalent 12·0, but in the ferric salts 20·1.

Again, in most of the vegetable acids, as in other organic compounds, hydrogen has a refraction equivalent of 1·3, but on examining hydrochloric, hydrobromic, and hydriodic acids, I was forced to the conclusion that it was exerting a far greater influence on light, an influence that had to be expressed by the number 3·5. This points to some radical difference in the constitution of these two classes of acids.

The so-called hydrochlorate of camphene (artificial camphor) gives a value composed of the ordinary values of carbon, hydrogen, and chlorine; and this lends great weight to the idea that it is not a compound of the essential oil with hydrochloric acid, $C_{10}H_{16}HCl$, but rather a new ternary compound, $C_{10}H_{17}Cl$; and with this its known reactions agree.

On the other hand, thymole, $C_{10}H_{14}O$, by giving a refraction equivalent much higher than the theoretical, is removed from the group of such substances as camphor, and placed along with its isomer carvole, and additional weight is given to that view which regards it as a homologue of phenylic acid, C_6H_6O.

In the table of carbon compounds given above, nitrogen was taken at 4·1, but ammonium in its salts is always about 11·6. Bearing this in mind, we may understand the following series, which otherwise would appear more irregular, indeed far beyond the limits of experimental error.

Compound.	Formula.	Condition.	Refraction equivalent.	
			Observed.	Calculated.
Bisulphide of carbon	CS_2	Liquid	36·7	37·0
Sulphocarbonate of ammonium	$CS_3(NH_4)_2$	Aqueous sol.	77·6	76·2
Sulphocarbamate do.	$CS_2NH_2NH_4$	do.	59·3	57·6
Xanthate of potassium	$KOCS_2C_2H_5$	do.	66·2	64·5

The greatest anomalies have been presented by oxygen. In organic compounds it was estimated by Landolt at 3·0, by myself at 2·9; but there are several oxidized hydrocarbons, such as thymole or anethole, which shew an enormous increase in refraction and dispersion. The estimates of oxygen from the following pairs of compounds are, on the contrary, less than 2·9, but they are not accordant with one another.

KNO_3	= 22·1	CO_2	= 10·03
KNO_2	= 19·3	CO	= 7·53
O	= 2·8	O	= 2·5
$KClO_3$	= 25·0	$KBrO_3$	= 31·4
KCl	= 18·8	KBr	= 25·1

O_3 = 6·2	O_3 = 6·3
O = 2·07	O = 2·1

The following series, however, give another aspect to the calculation.

Substance.	Formula.	Refraction equivalent.
Sulphide of Potassium	K_2S	34·6
Sulphite of Potassium	K_2SO_3	35·1
Hyposulphite of Potassium	$K_2S_2O_3$	47·9
Sulphate of Potassium	K_2SO_4	33·1

Here the equivalent of oxygen would seem to be rather a minus than a plus quantity! And this does not stand alone, for metaphosphoric acid has a smaller value than the phosphorus it contains.

Phosphorus	P	= 18·3
Metaphosphoric acid	PHO_3	= 18·0
Orthophosphoric acid	PH_3O_4	= 23·6

Similar indications are given by arsenic, stannic, and some other acids. This points to the general conclusion not so much that oxygen has several refraction equivalents, as that it has the power of greatly modifying the action on light of those elements with which it is combined in a high proportion.

On comparing the refraction equivalents in the table given above, it will strike most chemists that some of those well-known pairs of elements having the same, or nearly the same atomic weight, have also the same influence on light, as for instance iron and manganese. But these relations are more numerous when we consider the specific refractive energy of the elements instead of their refraction equivalents. Nor is this to be wondered at, for it is the energy that is the more characteristic physical property, seeing it expresses a simple fact, and is independent of theoretical views as to atomic weight. The following pairs may be noted:—

Iron	0·214	Aluminium	0·307
Manganese	0·222	Chromium	0·305

Nickel	0·177	Antimony ..	0·201
Cobalt	0·184	Arsenic	0·205

Bromine .. 0·191, or in salts 0·211
Iodine 0·193, do. 0·214

But the most interesting and suggestive comparison is that between the specific refractive energy and the combining proportions of those metals that form salts not decomposable by water. By combining proportions I do not mean the "atomic weights" or what are usually given as "chemical equivalents," but the actual amount which will combine with a certain quantity of a salt radical, say 35·5 of chlorine.

In the following table the metals are arranged according to the order of their energies, beginning with the highest.

Element.	Specific refractive energy.	Combining proportion.
Hydrogen	1300	1
Glucinium	606	4·7
Lithium	540	7
Aluminium	307	9·1
Chromium	305	17·4
Magnesium	292	12
Calcium	260	20
Zirconium	249	22·4
Rhodium	232	34·8
Manganese	222	27·5
Iron	214	28
Sodium	209	23
Palladium	208	26·6
Potassium	207	39·1
Cobalt	184	29·4
Copper	183	31·7
Nickel	177	29·4
Didymium	166	48
Rubidium	164	42·7
Zinc	156	32·6
Strontium	155	43·8
Cerium	148	46
Platinum	132	49·3
Silver	125	108
Gold	122	65·7
Cadmium	121	56
Lead	120	103·5
Barium	115	68·5
Mercury	107	100
Thallium	106	204
Cæsium	103	133
Uranium	90	120

It will be seen that while the numbers in the first column decrease, those in the second pretty steadily increase. Many of the energies will probably be modified on further investigation, but there are exceptions which are certainly not due to errors of experiment; chromium and potassium may be noticed, and the group silver, lead, and thallium, three elements having a certain chemical relationship, the combining proportions of which would have to be halved in order to bring them to about their right places in the list. Still the general significance of the table is not to be mistaken.

At first sight it might seem that the metal which was more powerful for doing one thing, was less powerful for doing another, but it should be remembered that a small combining proportion means a high saturating power. This relation between the two lists of numbers, though it has not the exactness which might be desired when we are tracing a physical law, points clearly to some connexion between the power of a metallic element to refract the rays of light, and its power to saturate the affinities of other bodies.

It may be remarked that these metallic elements do not differ from one another so widely in their optical as in their chemical quality, the first ranging only from 13 to 0·9, while the second varies between 1 and 204.

In future I hope to extend this investigation to all the elements, to settle those refraction equivalents which are still doubtful, and to examine the apparent exceptions, especially with a view to determine how far a change of atomicity is accompanied by a change of refractive energy; and, beyond all this, the question of dispersion offers an inviting, but as yet almost untrodden, field of enquiry.

Substance.	Equivalents of solvent.	Specific gravity.	Temp. centigrade.	Refractive indices.		
				A.	D.	H.
Hydrate of oil of turpentine.....	63·58 alcohol.....	0·819	9°	1·3690	1·3732	1·3846
Camphor.....	4·54 do.	0·866	8·5°	1·4022	1·4067	1·4205
Bihydrate of cajeput		0·916	20°	1·4532	1.4583	1·4745
Oil of wormwood		0·927	20°	1·4543	1·4598	1·4786
Sugar	9·10 water	1·340	7°	1·4588	1·4637	1·4771
Succinate of potassium	71·50 water + 0·28 $C_4H_6O_4$	1·093	9°	1·3517	1·3563	1·3679
Urea.....	7·00 water	1·088	25·5°	1 3762	1·3815	1·3952
Chloride of acetyl		1·159		1·3992	1·4042	1·4213
Chloropicrin		1·678	9°	1·4616	1·4679	1·4876
Hydrochlorate of camphene.....	37·92 alcohol.....	0·823	9°	1·3713	1·3757	1·3876
Iodoform.....	38·54 ether.....	0·820	9°	1·3671	1·3716	
Sulphocarbonate of ammonium ..	35·47 water	1·065		1·3918	1·3988	
Sulphocarbamate of ammonium ..	18·71 do.	1·091	10°	1·4171	1·4254	
Xanthate of potassium	24·34 do.	1·106	4°	1·3891	1·3961	
Chlorate of potassium	126·75 do.	1·032	17°	1·3334	1·3376	1·3483
Bromate of potassium	193·49 do.	1·035	17°	1·3341	1·3382	1·3491
Metaphosphoric acid.....	8·23 do.	1·270	20·5°	1·3718	1·3764	1·3879
Orthophosphoric acid	13·30 do.	1·180	7·5°	1·3584	1·3630	1·3746

XV.—*Researches on Kryptophanic Acid, the normal free acid of Human Urine.*

By J. L. W. Thudichum, M.D.

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1. *Mode of isolating Kryptophanic Acid from fresh Human Urine by Lime and Alcohol process.*

The urine is treated with milk of lime to alkalinity, filtered and evaporated. After filtration from the gypsum, it is acidified with acetic acid, and evaporated to crystallisation. After some standing, the syrup is filtered from the salt cake, and is now ready for treatment with alcohol. Of this syrup one volume is mixed with four volumes of alcohol of 95 per cent., or five volumes of 90 per cent., and shaken in a stoppered bottle. A voluminous, flaky, adhesive, dark precipitate is formed, which speedily settles in the bottom of the fluid. The liquor is decanted, the precipitate shaken with some fresh strong alcohol, and the alcohol again decanted. The bottle and precipitate

are now slightly warmed, when the latter gives out much alcohol, which is poured away.

The impure calcium salt is now dissolved in a small quantity of water, filtered through a calico bag with the aid of pressure (it soon clogs any paper filter), and again precipitated with four volumes of strong alcohol. The precipitate is collected in a calico bag, and freed from alcohol by pressure. It is now free from the soluble urinary ingredients. By repeating the solution in water and precipitation with alcohol a few times more, almost pure calcium kryptophanate can be obtained. But it is preferable to adopt one or other of the following processes of purification.

2. *Purification by Lead Acetate.*

The crude calcium salt, above described, is dissolved in water, and mixed with a large quantity of nearly saturated watery solution of neutral lead acetate. The mixture is shaken in a stoppered bottle, and filtered. The filtrate is nearly colourless; a dark-coloured voluminous precipitate of basic salt remains on the filter. The latter is washed with some saturated lead solution. The united filtrates, containing all the neutral lead kryptophanate in solution, are mixed with five or six volumes of alcohol of 95 per cent., whereupon perfectly white lead kryptophanate is deposited in flakes. They are washed with alcohol, slightly with water (for washing with much water produces basic salt), then with alcohol again, lastly, with ether, and dried *in vacuo*, during which they assume a slightly yellowish colour on the surface. The precipitate may also simply be washed with water, to remove lead acetate, the basic kryptophanate being also insoluble in water as well as in alcohol. By decomposition with the exact amount of sulphuric acid required, the free acid is obtained, and best transformed into baryum salt by baryta-water in excess and a current of carbonic acid. The baryum salt is precipitated by alcohol, redissolved in water, and again treated with lead acetate in excess. The filtrate with alcohol yields pure white kryptophanate. (The insoluble part is basic salt, and can be used for obtaining the free acid by decomposition with an equivalent quantity of dilute sulphuric acid.)

3. *Purification by Copper Acetate.*

To the solution of the crude calcium salt an excess of copper acetate is added. A voluminous dirty green precipitate ensues, and a greenish-blue solution forms, which is separated by filtration. To this latter five or six volumes of alcohol of 95 per cent. are added, which produce a voluminous greenish-blue flaky precipitate. This is filtered and washed with alcohol, and dried *in vacuo* over sulphuric acid. The mother-liquor must remain blue with excess of copper acetate, in order to obtain all kryptophanic acid as copper salt, free from calcium. This copper salt is soluble in water, while moist with alcohol, but insoluble in water after it has been dried. Its solution, before the addition of alcohol, must not be heated, as in that case a change takes place, as evidenced by the formation of an insoluble greenish-red precipitate. In order to obtain the free acid, the copper salt must be decomposed with sulphuretted hydrogen.

4. *Mode of obtaining Kryptophanic Acid from Urinary extracts after removal of all products of decomposition of Urochrome by Sulphuric Acid.*

In the foregoing process applied to fresh urine the urochrome remains undecomposed in the alcoholic solution. Kryptophanic acid is therefore not a product of urochrome, as is also evident from many other circumstances. In the process now to be described, kryptophanic acid is obtained in large amount from the extracts from which urochrome products have been entirely removed.

The extracts containing great quantities of ammonium sulphate are mixed with excess of milk of lime, filtered through cloths, and boiled to drive out all ammonia. They are then acidified with acetic acid, and evaporated to crystallisation. The filtered extract is treated with alcohol like the extracts from fresh urine. The precipitate contains much more potassium chloride than that from fresh urine, and requires special care to be purified from this by one or other of the above processes. It also contains iron, which follows the acid into nearly all its preparations. This is best removed by adding to the solution, freed from calcium by ammonia and ammonium carbonate, a sufficient amount of ammonium sulphide, and filter-

ing immediately. By evaporation the alkali and sulphide are removed, and the solution of the ammonium-salt is ready for the application of lead acetate.

5. *Mode of obtaining Kryptophanic Acid from fresh Urine without the intervention of Heat.*

The dilute free acid and its acid salts are little affected by heat and air, but its neutral and alkaline salts become dark in solution, or in the wet state. To avoid this objectionable effect the following process may be adopted. The filtered fresh urine is treated with lead acetate as long as this reagent produces a precipitate. An excess of neutral lead salt is to be carefully avoided. Experience shows that to every litre of the fresh urine of healthy men 40 cubic centimetres of a solution saturated at 9·5° C. of lead acetate should be added, and the precipitate produced thereby will be sulphate and phosphate exclusively, with only a trace of organic salt. (From 1 litre of average urine 6·2 grm. of mixed lead salts are obtained.) To the filtrate more acetate and some ammonia are added. The precipitate is collected in a calico-bag, pressed, washed with water, pressed again, and then decomposed with sulphuric acid in slight excess. It is yellow, and gives the spectrum of urochrome, being a broad absorption band at the beginning of blue. The filtrate is treated with baryum carbonate and a little baryta water. The solution of baryum kryptophanate is now mixed with five volumes of nearly absolute alcohol, whereupon the kryptophanate is precipitated, the urochrome remaining in solution. The baryum kryptophanate is dissolved in water, and again precipitated with lead acetate ; the precipitate, after filtration, is digested with a sufficiency of saturated solution of lead acetate and the solution filtered. The filtrate is treated with five volumes of nearly absolute alcohol, whereupon lead kryptophanate falls down in white flakes which should be washed with alcohol, a little water, alcohol again, lastly with ether, and dried *in vacuo*.

6. *Properties of Kryptophanic Acid.*

It is a transparent, amorphous, gummy, solid mass, almost or entirely colourless. It is soluble in water in all proportions; less soluble in alcohol. Alcohol produces a precipitate in

the water solution, and after this has deposited, ether produces a new precipitate in the mixture. It has a freely acid taste. It decomposes the carbonates of alkalies and earths with effervescence, forming watery solutions of the salts. Its solution forms, with lead acetate, a copious thick white precipitate; with mercury acetate a similar precipitate; with silver nitrate the precipitate is slight.

The lead acetate precipitate forms a clear solution with excess of acetate. The solution of the free acid is not precipitated by mercury dichloride, nor by copper acetate.

The aqueous solutions of its earthy salts show the following reactions:—

They are precipitated by excess of alcohol. On being heated they fuse and become dark, ultimately dry, and may be powdered, after which they are very stable. Boiled with a great excess of alkaline copper solution they reduce the oxyde and form suboxyde, which remains in solution, but is deposited if the mixture is concentrated and air excluded. The alkaline solution fluoresces blue.

The watery solutions of the earthy salts are precipitated copiously white by lead acetate, and are soluble in excess of acetate; by mercury acetate, white; by mercury nitrate, voluminous white; the ordinary estimation of urea by this reagent is thus shown to be liable to error and to require a correction for kryptophanic acid, which has probably increased all values obtained for urea by from 5 to 10 per cent.; by silver nitrate, white voluminous. All these precipitates are slightly soluble in water, insoluble in alcohol; they are soluble in nitric acid.

Iodine, dissolved in an iodide, on being added to a solution of kryptophanic acid or of a kryptophanate, produces immediately an iodo-kryptophanic acid, in which one or several atoms of hydrogen are replaced by iodine. The liquid immediately contains hydriodic acid. Thus, on addition of tincture of iodine to fresh urine, the iodine is at first precipitated, as if the tincture had been added to water, but is almost immediately redissolved by substituting hydrogen in kryptophanic acid. This reaction was the subject of a lively debate in France some years ago.

Bromine added to kryptophanic acid, or the solutions of its salts in water, immediately produces a brominated acid, in which one or more atoms of hydrogen are replaced by bromine.

The reaction with bromine is perhaps neater than that with iodine, and the product less liable to change and decomposition.

The kryptophanates on being heated, emit acid vapours, but no urinary smell whatever is perceived, like that emitted by omicholine. They then leave a quantity of charcoal, which requires prolonged heating before it is entirely consumed. Kryptophanic acid prevents the precipitation of ferric oxide from solutions containing excess of caustic alkali. Like oxalic acid, it holds prussian blue in solution, in the presence of free hydrochloric acid.

An ammoniacal silver nitrate solution becomes immediately very dark on addition of ammonium kryptophanate. On standing it becomes apparently black (being red when diluted), and deposits metallic silver as a black powder.

Nitrate of silver and excess of nitric acid, added to a solution of kryptophanic acid containing urea (to urine with little urochrome and much Kr, such as is discharged in certain conditions of the brain, intermittent spasmodic disease), is reduced on standing, and the glass is covered with a silver mirror.

7. *Absorption of Oxygen by Crude Kryptophanic Acid in Alkaline Solution.*

A quantity of crude kryptophanate of calcium was dissolved in water to 20 c.c., and enclosed in a graduated tube over mercury; 47 c.c. of air were now allowed to enter the tube, and after that 14 c.c. of concentrated caustic potash solution were added. After three weeks of standing, the air had diminished to 38 c.c., so that 9 c.c. of oxygen had been absorbed, equal to to 19·1 per cent. of the air employed.

When highly purified, neither the free kryptophanic acid, nor its baryum salt with excess of baryta water, seem to absorb pure oxygen over mercury.

8. *Kryptophanates of the Alkalies.*

These salts are very soluble in water.

The sodium-salt is not precipitated from its aqueous solution by alcohol.

9. *Kryptophanate of Lead*, $C_5H_7PbNO_5$.

Crude calcium kryptophanate, precipitated by alcohol, was mixed with excess of a saturated solution of lead acetate, and filtered from the precipitate of basic kryptophanate.

The solution was mixed with five volumes of alcohol of 95 per cent. The precipitate of kryptophanate, a white flaky mass, thereby produced, was washed with alcohol, water, alcohol, and ether, in succession, and dried *in vacuo*. It darkened during the washing, and ultimately became pale yellowish. When quite dry it had shrunk very much, and acquired a dark colour.

Analysis (dried *in vacuo*) :—

I. ·3996 grm., with H_2SO_4 and ignition, yielded ·3104 $PbSO_4$, equal to 53·07 per cent. Pb.

The formula $C_5H_7NPbO_5$ + aq., requires 53·62 per cent. Pb.

The above lead salt which had been kept over sulphuric acid, was now further dried at 105°.

(Exposed to the air this salt absorbed nearly the whole of its water, and on again drying lost it again.)

Analysis of the salt dry at 105° :

I. ·5900 yielded ·4820 grm. $PbSO_4$, which, allowing ·0008 for correction, gives 55·72 per cent. Pb.

II. Combustion—1·3905 burned with CuO, etc., gave ·2363 H_2O, and ·800 CO_2, equal to 1·89 per cent. H, and 15·69 per cent. C.

III. Nitrogen determination—·7708 grm. burned gave gas equal to 21·48 c.c. normal (*i.e.*, at 0°, 760 mm. and dry). After oxygen and pyrogallate of potassium, it gave gas = 13·97 c.c. normal, therefore nitrogen = 17·73 c.c., or 0·2226 grm., or 2·89 per cent.

IV. ·5847 gave ·4760 $PbSO_4$, equal to 55·73 per cent. Pb.

	Calculated.		Found.			
			I.	II.	III.	IV.
5 C	60	16·30	—	15·69	—	—
7 H	7	1·90	—	1·89	—	—
Pb.....	207	56·25	55·72	—	—	55·73
N	14	3·80	—	—	2·89	—
5 O	80	21·75				
	368	100·00				

10. *Basic Lead Kryptophanate.*

When the neutral salt is washed with water for a long time it loses one-third of its acid, and there remains behind a salt having the composition $2(C_{10}H_{14}Pb_2N_2O_{10})PbO$.

	Theory.		Found.		
			I.	II.	III.
20 C	240	14·16	13·05	—	—
28 H	28	1·65	1·75	—	—
5 Pb	1035	61·06	—	61·2	60·61
4 N	56				
21 O	336				
	1695				

Note.—Analyses 1 and 2 on the same preparation. Analysis 3 on sample prepared in another operation.

11. *Kryptophanate of Copper* (*with alcohol*).

Prepared by adding a great excess of copper acetate to a solution of the calcium or sodium salt, filtering and precipitating the filtrate with much alcohol, washing with alcohol, and drying in the steam-oven, powdering, drying *in vacuo*. Prepared in this way the salt is a compound of kryptophanate with alcohol.

Analyses :—

I. Combustion with oxide of copper, a little potassium chlorate, and copper turnings.

1·2771 burned gave ·5305 H_2O, and 1·3555 CO_2 equal to 4·62 per cent. H., and 28·95 per cent. C.

II. ·4885 burned as I, gave ·2100 H_2O, and ·5290 CO_2 equal to 4·67 per cent. H, and 29·53 per cent. C.

III. ·7235 burned and treated with HNO_3 gave ·2192 CuO, equal to 24·20 per cent. Cu.

IV. ·4470 gave CuO ·1384, equal to 24·67 per cent. Cu.

V. In this analysis 24·18 per cent. Cu were obtained.

	Found.				
	I.	II.	III.	IV.	V.
C	28·95	29·53	—	—	—
H	4·62	4·67	—	—	—
Cu.....	—	—	24·20	24·67	24·18

The analyses lead to either $2(C_5H_7CuNO_5) + C_2H_6O$, or $2(C_5H_7NCuO_5) + C_2H_6O + H_2O$.

12. *Kryptophanate of Copper* (*without alcohol*), $C_5H_7CuNO_5$.

If the foregoing salt is exposed to moist air, and then dried *in vacuo*, it loses *alcohol*, and at the same time changes in colour, becoming very dark green.

Analysed in that state it yields results corresponding with the formula $C_5H_7NCuO_5$.

Analyses:—

I. Combustion with copper oxide, potassium chlorate, and Cu.

·2859 gave ·2840 CO_2, equal to 27·09 per cent. C. (water not weighed).

II. Nitrogen determination—·4016 gave ·0255 grm. of N., equal to 6·35 per cent.

III. ·1752 grm. gave ·0603 CuO, equal to 27·50 per cent. Cu.

IV. Dried at 120° ·4077 left ·1455 CuO, equal to 28·82 per cent. Cu.

	Calculated.		Found.			
			I.	II.	III.	IV.
C_5	60·	26·72	27·09	—	—	—
H_7	7·	3·12	—	—	—	—
Cu	63·5	28·29	—	—	27·50	28·82
N.....	14·	6·24	—	6·35	—	—
O_5	80·	35.63				
	224·5	100·00				

Dry Distillation of Copper Salt.—8·25 grm. of this salt was subjected to dry distillation, and yielded, first water, which was removed from the receiver; then, on stronger heating, a white heavy vapour came over, which was alkaline, smelled of cyanide, and of tobacco, and crystallised in white crystals on cooling. It

was perhaps cyanide and cyanate of ammonium, effervesced with platinum tetrachloride, and gave a crystalline salt; it was accompanied with a dark red oil, which, when mixed with HCl and $PtCl_4$ reduced the platinum, and gave a rather black solution. The oil was more soluble in ether than the crystals, so that a separation could be thereby effected.

13. *Kryptophanate of Magnesium.*

Free acid, prepared by the decomposition of wet lead-salt by means of an equivalent of dilute sulphuric acid, was treated with an excess of magnesia, filtered, and the filtrate evaporated on the water-bath.

The salt formed a mass like treacle, which was dried up, powdered, and dried at 110° to 120°.

Analyses :—

I. ·5363 grm. ignited gave ·1023 grm. MgO equal to 11·45 per cent. Mg.

II. Dried at 125° for some time, ·508 grm. salt left after combustion ·100 grm. MgO, equal to 11·8 per cent. Mg.

III. ·4653 grm. gave ·0893 MgO, equal to 11·51 per cent. Mg.

IV. ·5232 grm. gave ·03484 grm. nitrogen, equal to 6·66 per cent. N.

	Calculated.		Found.			
			I.	II.	III.	IV.
10 C.....	120	29·56	—	—	—	—
14 H	14	—	—	—	—	—
2 Mg....	48	11·83	11·45	11·81	11·51	—
2 N	28	6·90	—	—	—	6·66
10 O.....	160					
2 Aq	36					
	406					

Dried at from 140° to 160° it lost an atom of water, and became $C_{10}H_{14}Mg_2N_2O_{10}+Aq$.

Theory.		Found.	
		I.	II.
30·93	C	31·01	—
4·12	H	4·78	—
12·37	Mg	—	12·12

I. Combustion ·3650 grm. gave ·1570 grm. H_2O, and ·415 CO_2, equal to 4·78 per cent. H., and 31·01 per cent. C.

II. ·4690 grm. gave ·0948 grm. MgO, equal to 12·12 per cent. Mg.

14. *Calcium Kryptophanates.*

Some free acid was made by decomposing lead salt with an equivalent of dilute H_2SO_4 (a little baryta water was added to remove a slight excess of sulphuric acid). An excess of milk of lime, prepared from lime which had been washed, was added to the acid, and the mixture boiled and filtered. To the filtrate about an equal volume of strong alcohol was added, and a precipitate obtained. This was dried in the water-bath, further dried at 110°, and analysed.

I. ·6242 grm. gave ·3152 grm. $CaSO_4$, equal to 14·85 per cent. Ca.

Further dried at 170°.

II. ·2845 grm. gave ·1465 grm. $CaSO_4$, equal to 14·92 per cent. Ca.

III. ·6240 grm. burned with lead chromate gave ·7542 CO_2 equal to 33·14 per cent. C.

The filtrate was evaporated to dryness, and the lime-salt powdered and dried at 135°.

Analysis:—

IV. ·348 grm. gave ·2002 grm. $CaSO_4$, equal to 16·94 per cent.

	Theory.		Found.			
			I.	II.	III.	IV.
10 C	120	32·88	—	—	33·14	—
13 H	13	—	—	—	—	—
½ Ca....	60	16·43	14·85	14·92	—	16·95
2 N	28					
9 O	144					
	365					

When kryptophanic acid is boiled with excess of milk of lime, there is produced a salt containing ½ of Ca to 1 of acid. This salt has considerable stability, but appears to be very slowly

attacked by the CO_2 of the air. If, however, the salt be dried up and then powdered, one-third of the calcium passes into carbonate, and the dibasic salt $C_{10}H_{14}CaN_2O_9$ is produced (just as in the case of the Ba salt).

15. *Kryptophanate of Baryum.*

The magnesium salt was precipitated boiling with slight excess of hydrate of baryum, filtered, and evaporated nearly to dryness in the water-bath; refiltered, and the filtrate dried in the water-bath. It formed a perfectly translucent red-brown varnish. Dried at 110°.

Analysis :—

I. ·445 grm. gave ·338 grm. $BaSO_4$, equal to 44·66 per cent. Ba.

$C_{10}H_{14}Ba_2N_2O_{10}$ + Aq. requires 44·62 per cent. Ba.

This salt took up CO_2 of the air, and formed a deposit of $BaCO_3$. The solution on evaporation to dryness left a residue, which dried at 110°, contained 36·28 per cent. Ba.

It would also seem that there is a baryta-salt of the formula $C_{10}H_{15}Ba_{\frac{3}{2}}N_2O_{10}$.

16. *Metamorphosis of Baryum Kryptophanate into an Acid Salt by boiling with water.*

15·5 grammes of copper kryptophanate (containing a certain quantity of alcohol) was decomposed with hydrogen sulphide and filtered. The filtrate was boiled for a long time with baryum carbonate and some baryum hydrate, and gave off a smell of ammonia. It was subsequently filtered. The precipitate on the filter contained much carbonate, and probably an organic product of decomposition. The filtrate was mixed with a large quantity of 98 per cent. alcohol, whereupon a pale yellowish white baryum salt was precipitated. This salt was washed with alcohol of 98 per cent. (the wash-alcohol was strongly alkaline), dissolved in water, and the aqueous solution boiled. Thereupon ammonia was again perceptible, and an abundance of baryum carbonate precipitated. This was removed by filtration, the filtrate evaporated to dryness at 110° and powdered. It

formed a gummy mass, offering no difficulty to comminution. The total amount of baryum salt obtained was 4·377 grms.

Analyses:—

I. ·5170 grm. burned with lead chromate and copper turnings gave ·1800 H_2O and ·5090 CO_2, equal to 3·87 per cent. H., and 26·94 per cent. C.

II. ·4025 grm. gave ·02391 grm, nitrogen, equal to 5·94 per cent. N.

III. ·2700 grm. dried at 110°, and burned, left ·1458 $BaSO_4$, equal to 31·75 per cent. Ba.

These data lead to the formula $C_{10}H_{14}BaN_2O_9$:

	Calculated.		Found.		
			I.	II.	III.
10 C	120	27·09	26·84	—	—
14 H.....	14	3·16	3·87	—	—
Ba	137	30·93	—	—	31·75
2 N.....	28	6·32	—	5·94	—
9 O.....	144	32.50	—	—	—
	443	100·00			

The reaction by which this salt is produced is the loss of baryum oxide. Thus:

	C_5	H_7	Ba	N	O_5
+	C_5	H_7	Ba	N	O_5
	C_{10}	H_{14}	Ba_2	N_2	O_{10}
−			Ba		O
	C_{10}	H_{14}	Ba	N_2	O_9

This salt gave a white precipitate with silver nitrate, soluble in nitric acid. It gave a white precipitate with lead acetate soluble in acetic acid. It gave no reaction with copper acetate, zinc chloride, or calcium chloride. With corrosive sublimate it gave a white precipitate soluble in HNO_3; with mercuric nitrate the same; with mercurous nitrate a precipitate which apparently white at first became quickly dark. The solid baryum salt, moistened with strong sulphuric acid, appeared to give a double sulphate and kryptophanate of baryum.

17. *Kryptophanates of Cobalt.*

A solution of kryptophanic acid (some of the same sample as that employed for magnesium salt) was treated with cobalt carbonate; effervescence ensued in the cold and more on boiling. A red solution was obtained and precipitated by two volumes of alcohol of 94 per cent. A pale pink precipitate ensued, which was filtered off. On drying in the steam-bath it shrunk, then fused like the calcium and other salts, and soaked the paper like fat (of this the greater portion dissolved in warm water with red colour as before). It ultimately became hard, and then was white rose coloured in the interior of the lumps. It was powdered and dried at 100° to 110°.

Determination of Co.—·0834 grm. burned and reduced in H atmosphere gave ·014 grm. or 16·78 per cent Co. The formula $C_{10}H_{16}CoN_2O_{10}$ (M.W. 382·8) requires 15·36 per cent. Co.

The formula $C_{10}H_{14}CoN_2O_9$ requires 16·19 per cent. Co.

Solution in Alcohol.—Was of a rose red colour, and on evaporation in platinum dish, became indigo blue wherever it dried, and was ultimately a deep blue hard mass. It was redissolved in water, when it again became red; filtered from slight precipitate and again evaporated. Dried at 110°. On heating it swelled up greatly, gave out stinking gas, and left residue of cobalt and carbon. This had to be treated with nitric acid to deflagrate all carbon, after which the cobalt was reduced in hydrogen atmosphere.

Determination of Cobalt.—·2897 grm. left after the before mentioned treatment ·08 grm. Co or 27·7 per cent. Co. The formula $C_{10}H_{14}Co_2N_2O_{10}$ (M.W. 439·6) requires 26·7 per cent. Co. $C_{10}H_{12}Co_2N_2O_9$ requires 27·9 per cent. Co.

18. *Silver-salts.*

When a solution of a tetrabasic kryptophanate, as for instance the magnesium salt, $C_{10}H_{14}Mg_2N_2O_{10}$, is mixed with a solution of silver nitrate, there is produced a dark grey precipitate, which either has not a definite composition or else suffers decomposition spontaneously or on washing. The following determinations of silver in different specimens of the precipitate will serve to illustrate the inconstancy of its composition after having been washed and dried.

	Percentage of silver.
Precipitate *a*	77·2
Do. *b*	60·08
Do. *c*	56·56

Precipitate *a* was prepared by using *a very small proportion* of silver nitrate to precipitate the magnesium kryptophanate. It was washed, dried in the steam-bath, and finally dried at 100° to 110°

Precipitate *b* was washed six times with a small quantity of water and dried in vacuo.

Precipitate *c* was very little washed, and then pressed and dried in vacuo for several days.

Thus it appears that by dint of washing decomposition of the silver-salt is effected, so as to give a salt richer in silver than the original precipitate.

Precipitate *c*, which may be regarded as the least altered specimen of the precipitated silver-salt, roughly approximates in composition to the formula $C_{10}H_{14}Ag_4N_2O_{10}+2$ Aq., corresponding with the magnesium-salt from which it was formed. The following are the details of its preparation and analysis:—

3 grm. of silver nitrate were dissolved in water and precipitated with 8 c.c. of very concentrated solution of tetrabasic magnesium kryptophanate. The dark-coloured precipitate, after slight washing, pressing, and drying *in vacuo* for several days, weighed 1·603 grm.

I. ·8455 grm. burnt with copper oxide, etc., gave ·4055 grm. of CO_2 (water not weighed).

II. ·4300 grm. gave ·2432 grm. of metallic silver (by ignition after moistening with nitric acid).

The formula $C_{10}H_{14}Ag_4N_2O_{10}+2$ Aq. requires

	Calculated.		Found.
10 C	120	15·2	13·08
18 H	18	—	—
4 Ag	432	54·7	56·56
2 N	28		
12 O	192		
	790		

(It will be understood that the insufficiency of the washing would occasion the carbon to be too low, and the ignited residue to be too high for the real quantity of silver.)

The interpretation which is to be put on the data given by this examination of the silver-salt appears to be the following. The tetrabasic silver-salt is very perishable, and breaks up into tribasic silver-salt and silver oxide. By washing, tribasic silver-salt is more or less perfectly dissolved out, and silver oxide accordingly accumulates in the precipitate.

The stable silver-salt of kryptophanic acid appears to be the tribasic salt, and is formed by double decomposition, when either a dibasic or a tribasic kryptophanate is added to a solution of silver-nitrate. It is white, and appears to be rather soluble in water.

a. Some silver-salt obtained by double decomposition between dibasic calcium-salt and silver nitrate, was washed and dried in vacuo. ·1110 grm. gave ·0570 grm. of metallic silver, or 51·35 per cent. Ag.

b. Some silver-salt prepared from dibasic baryum-salt and silver-nitrate, and dried in vacuo, gave 52·80 per cent. Ag.

c. Another quantity of silver-salt made from a specimen of calcium kryptophanate, believed to be the tribasic salt, had the following history :—

Calcium kryptophanate, purified twice by resolution in water, and precipitation by alcohol, was boiled with animal charcoal to decolorize it, and then mixed with silver nitrate as long as a precipitate was produced. The precipitate, white at first, became slightly coloured grey. It was washed, ultimately boiled with alcohol, and dried at 100° to 110°. At 130° it became brownish on surface.

Analyses :—

I. ·2785 grm. left ·1479 grm. or 53·1 per cent. Ag.

II. ·3722 grm. left ·2005 grm. or 53·86 per cent. Ag.

III. 52·8 per cent. Ag. found.

IV. ·2048 grm. burned with CuO, Cu, and $KClO_3$, yielded ·150 of CO_2 and ·046 H_2O, equal to ·0409 grm., or 19·97 per cent. C., and ·0051 grm. or 2·49 per cent. of H.

V. ·2656 grm. burned with CuO and Cu gave gas = 16·1 c.c. at 12·5° and 641·2 mm. (dry), equal to 13· c.c. absolute. Corrected with O for NO this became 12· c.c. absolute, equal to ·01507 grm., or 5·7 per cent. N (roughly).

	Calculated.		Found.						
			a.	*b.*	I.	II.	III.	IV.	V.
10 C	120	19·08	—	—	—	—	—	19·97	—
13 H	13	2·07	—	—	—	—	—	2·49	—
3 Ag	324	51·53	51·35	52·80	53·1	53·8	52·8	—	—
2 N	28	4·45	—	—	—	—	—	—	5·7
9 O	144								
	629								

19. *Theoretical considerations on Kryptophanic Acid.*

Kryptophanic acid is written in much of the foregoing as a dibasic acid of the formula $C_5H_9NO_5$. But it is evident that it may be considered as tetrabasic, and to have the formula $C_{10}H_{18}N_2O_{10}$. In that case the metallic salts will have the general formula $C_{10}H_{14}M'_4N_2O_{10}$.

Examples:—

Lead-salt	$C_{10}H_{14}Pb_2N_2O_{10}$.
Do. hydrated.....	$C_{10}H_{14}Pb_2N_2O_{10} + 2Aq.$
Basic	$2(C_{10}H_{14}Pb_2N_2O_{10})PbO.$
Copper salt	$C_{10}H_{14}Cu_2N_2O_{10}$.
Do. with alcohol	$C_{10}H_{14}Cu_2N_2O_{10} + C_2H_6O.$
Magnesium salt.....	$C_{10}H_{14}Mg_2N_2O_{10} + Aq.$
Do. dihydrate	$C_{10}H_{14}Mg_2N_2O_{10} + 2Aq.$
Baryum salt	$C_{10}H_{14}Ba_2N_2O_{10} + Aq.$
Do. tribasic	$C_{10}H_{13}ba^I{}_3N_2O_{10}$.
Do. acid.....	$C_{10}H_{14}BaN_2O_9$.
Calcium salt	$C_{10}H_{13}ca^I{}_3N_2O_9$.
Do. acid.....	$C_{10}H_{14}CaN_2O_9$.
Cobalt-salt, acid.....	$C_{10}H_{14}CoN_2O_9$.
Do. basic	$C_{10}H_{12}Co_2N_2O_9$.
Silver-salt	$C_{10}H_{13}Ag_3N_2O_9$.

It gives me great pleasure to acknowledge the important aid which I have received from my friend Mr. J. A. Wanklyn in the latter part of this research, more particularly in the elucidation of the changes of basicity of several salts.

My thanks are also due to my assistant Mr. C. G. Stewart, for the care and assiduity with which he prepared for me large quantities of the primary material.

The foregoing research has been conducted by me for the Medical Department of the Privy Council, at the Pathological Laboratory of St. Thomas's Hospital.





XVI.—*On Artificial Alizarin.*

By W. H. Perkin, F.R.S.

In the remarks I have the honour of bringing before the Society, I thought it as well not only to give an account of what is actually new in reference to my subject, but at the same time, though in a very brief manner, to refer to a few points in the chemical history of alizarin and the researches which led to its artificial formation.

Alizarin was first obtained from madder in a crystalline condition by Robiquet and Colin, but the method they adopted for its preparation, viz., sublimation, rendered it a matter of uncertainty whether alizarin pre-existed in that substance or was a product of the decomposition of some other body. Dr. Schunck, however, after much labour, succeeded in obtaining it in a well crystallized state without having recourse to sublimation.

There has been a great deal of controversy respecting the formula of alizarin, Schunck contending for that which he first gave, viz., $C_{14}H_{10}O_4$, whilst Strecker believed it to be $C_{10}H_6O_3$, and related to Laurent's chloroxynapthalic acid, since both these substances yield phthalic acid by decomposition with nitric acid.

In fact, chloroxynaphthalic acid was regarded as chlorinated alizarin, the two bodies being thus related.

$C_{10}H_6O_3$	$C_{10}H_5ClO_3$
Alizarin or Oxynaphthalic acid.	Chlorinated alizarin, or Chloroxynaphthalic acid.

Of these formulæ, Strecker's became the favourite one.

About five years since Martius and Griess, when investigating the amide derivatives of naphthol, obtained a colouring matter possessing Strecker's formula. This, however, was not alizarin, but was regarded as an isomer of that body.*

Some time after the discovery of this supposed isomer of alizarin, Charles Graebe commenced his research on quinone.

* Annales der Chemie und Pharmacie, cxxxiv, p. 375. Bull. Chem. Soc., Paris, iv, p. 389.

This substance was discovered as early as 1838 by Woskresensky as a product of the oxidation of quinic acid, and although investigated by many chemists, as Wöhler, Laurent, Hofmann, Stenhouse, and others, no clue to its chemical structure had been obtained.

Kekulé, however, expressed the opinion that it might be a compound containing carbonyl, and represented thus:—

$$CO{=}CH{-}CH{=}CH{-}CH{=}CO$$
$$CO{=}C_4H_4{=}CO.$$

Graebe, after working with great energy upon quinone compounds, came to the conclusion that it is not constituted according to the above formula, but is a substitution-product of benzol in which two atoms of hydrogen are replaced by the group $(O-O)''$, in which half the combining values of oxygen saturate each other,* thus:—

C_6H_6	$C_6H_4(O_2)''$
Benzol.	Quinone.

The best known derivative of quinone is perhaps chloranil, or perchloroquinone. This is obtained by heating phenol with potassic chlorate and hydrochloric acid, its composition being

$$C_6Cl_4O_2, \text{ or } C_6Cl_4(O_2)''.$$

When heated with alkalies, it gives up two atoms of chlorine, and forms potassic chloranilate or dichloroquinonate.

$$\underset{\text{Chloranil.}}{C_6Cl_4(O_2)''} + 4KHO = \underset{\text{Potassic chloranilate.}}{C_6Cl_4\begin{cases}(O_2)''\\KO\\KO\end{cases}} + 2KCl + 2H_2O$$

When Graebe commenced his researches, no analogous substance to quinone connected with any other hydrocarbons than benzol was recognized; but after observing the relation of this substance to its hydrocarbon, this chemist was induced to view Laurent's chloride of chloroxynaphthyl as the dichlorinated quinone of naphthalin; bichloronaphthoquinone thus:—

$C_{10}H_8$	$C_{10}H_4Cl_2(O_2)''$
Naphthalin.	Bichloronaphthoquinone.

* Bull Soc. Chim., Paris, xi, p. 323.

This napthalin derivative, when heated with caustic alkalies, behaves in a somewhat similar manner to chloranil, part of the chlorine being removed; but in this case the reaction is limited to one atom of chlorine.

$$C_{10}H_4Cl_2(O_2)'' + 2KHO = C_{10}H_{10}Cl\left\{\begin{matrix}(O_2)''\\KO\end{matrix}\right. + KCl + H_2O$$

Dichloronaphthoquinone. Potassic chloroxynaphthalate.

The acid obtained from this salt, which has been assumed (as already stated) to be chlorinated alizarin, is a colouring matter, dyeing wool a scarlet or orange colour, but has no affinity for alumina mordants.

Jointly with M. Borgmann, Graebe obtained chlorinated quinones of toluol by heating cresylic acid with chlorate of potassium and hydrochloric acid. The following are the products obtained in this manner:—

$$C_6\left\{\begin{matrix}CH_3\\(O_2)''\\Cl_3\end{matrix}\right. \qquad C_6\left\{\begin{matrix}CH_3\\(O_2)''\\Cl_2\\H\end{matrix}\right.$$

Trichlorotoluquinone. Dichlorotoluquinone.

After it had been shown that chloroxynapthalic acid was a quinone acid, Graebe and Liebermann thought it probable that alizarin belonged to the quinone series; but before this could be proved it was necessary to get some clue to the hydrocarbon to which it is related. To obtain this information natural alizarin was taken and heated with powdered zinc, according to Baeyer's method of reducing aromatic compounds. In this manner they obtained a substance having the composition

$$C_{14}H_{10}.$$

This hydrocarbon formed a red compound with picric acid, and in fact possessed all the properties of anthracene as obtained from coal tar.

Graebe and Leibermann did not allow this discovery to rest, and reasoning from the information which had been obtained by the study of the quinones, they assumed alizarin to be the quinone acid of anthracene, thus—

$C_{14}H_{10}$ — Anthracene.

$C_{14}H_8(O_2)''$ — Anthraquinone.

$C_{14}H_6\left\{\begin{matrix}(O_2)''\\HO\\HO\end{matrix}\right.$ — Anthraquinonic acid. Alizarin.

It will be seen that this formula $C_{14}H_8O_4$ corresponds closely to that persisted in by Dr. Schunck, differing only by H_2.

Having obtained anthracene from alizarin, it now remained to produce alizarin from anthracene.

The first step in this process was to obtain the quinone.

Many years ago Laurent obtained an oxygenated derivative of anthracene, and named it *anthracenuse*. Dr. Anderson re-examined this body and gave it the formula $C_{14}H_8O_2$, and called it *oxanthracene*.

Graebe and Liebermann at once recognized this as the desired quinone of anthracene, or anthraquinone; it therefore only remained to convert this into the acid by replacing two atoms of its hydrogen by hydroxyl, and thus settle the question as to whether alizarin be the quinone acid of anthracene or not.

For this purpose anthraquinone was heated with bromine, and by this means dibromanthraquinone was obtained.

$$C_{14}H_8(O_2)'' + 4Br = C_{14}H_6\left\{\begin{matrix}(O_2)''\\Br_2\end{matrix}\right. + 2HBr.$$

I have referred to the decomposition of chloranil or tetrachloroquinone by potassic hydrate, how two atoms of chlorine are removed and potassic chloranilate is formed. It was therefore probable that dibromanthraquinone would decompose in a similar manner when treated with this re-agent. No decomposition, however, was found to take place until a temperature of about 180° C. was employed. The mixture of dibromanthraquinone and potassic hydrate then changed colour, becoming blue, and more and more intense, and when dissolved in water was found to be an alkaline solution of alizarin, which, when acidified, deposited this product as a yellow precipitate.

The reaction may be written thus :—

$$C_{14}H_6\left\{\begin{matrix}(O_2)''\\Br\\Br\end{matrix}\right. + 4KHO = C_{14}H_6\left\{\begin{matrix}(O_2)''\\KO\\KO\end{matrix}\right. + 2KBr + 2H_2O.$$

Dibromanthaquinone. — Potassic alizarate.

The latter product, when heated with hydrochloric acid, yielding hydric alizarate or alizarin.

$$C_{14}H_6\begin{cases}(O_2)''\\HO\\HO\end{cases} = C_{14}H_8O_4.$$

Thus Graebe and Liebermann succeeded in producing alizarin from anthracene, and have given us the first instance of the artificial formation of a vegetable colouring matter.

The great importance of alizarin as a dyeing agent rendered it desirable to turn this beautiful discovery to practical account, and, if possible, render alizarin from anthracene a substitute for madder. The use of bromine in Graebe's and Liebermann's process rendered it however somewhat difficult to carry out on a manufacturing scale; therefore it was necessary to find a cheaper and more manageable reagent which might be used in its stead.

It is well known that sulphuric acid forms with many organic bodies compounds called sulpho-acids. In composition these simply correspond to the substance acted upon, *plus* sulphuric anhydride, the basicity of the product (if derived from a neutral body) increasing with the number of molecules of sulphuric anhydride used in its formation.

It is found, however, that these so-called sulpho-acids are nothing more than acid sulphites; and we find sulpho-benzolic acid and disulpho-naphthalic acids are thus constituted:—

$$C_6H_6SO_3 = C_6H_5HSO_3.$$

Sulphobenzolic acid. Phenyl sulphurous acid.

$$C_{10}H_8 2SO_3 = C_{10}H_6\begin{cases}HSO_3.\\HSO_3.\end{cases}$$

Disulpho naphthalic acid. Naphthylene disulphurous acid.

The experiments of Würtz and Kekulé have confirmed this view of the constitution of these acids. They found that sulpho-benzolic acid, when heated with potash, produced a phenate and sulphite, thus:

$$C_6H_5HSO_2 + 3KHO = C_6H_5KO + K_2SO_3 + 2H_2O.$$

Sulphobenzolic acid. Potassic phenate.

M. Dusart also found that disulphonaphthalic acid yielded in the same way a naphthylenate and a sulphite.

$$C_{10}H_6\begin{cases}HSO_2\\HSO_3\end{cases} + 6KHO = C_{10}H_6\begin{cases}KO\\KO\end{cases} + 2K_2SO_3 + 2H_2O.$$

Disulphonaphthalic acid. Potassic naphthylenate.

By the addition of an acid to the product of these reactions, we obtain first from benzole, by means of the sulpho-acid, phenic acid or hydrate of phenyl, and from naphthalin naphthylenic alcohol or dihydrate of naphthalyne:

C_6H_6 C_6H_5HO $C_{10}H_8$ $C_{10}H_6\begin{cases}HO\\HO\end{cases}$

Benzol. Hydrate of phenyl. Naphthalin. Dihydrate of Naphthylene.

We thus see in the second example that we have obtained a body standing to naphthalin as alizarin does to anthraquinone.

It therefore appeared probable that if a disulpho-acid of anthraquinone could be found, alizarin might possibly be obtained by a similar process.

The formation of a sulpho-acid of anthraquinone, however, did not at first appear very probable, on account of the remarkable stability of this compound; nevertheless, after numerous experiments, it was found that when heated strongly with sulphuric acid, it disappeared, the mixture at last becoming perfectly soluble in water, a sulpho-acid having formed.

The analysis of salts of this new acid showed that it possessed the formula—

$$C_{14}H_6\begin{cases}(O_2)''\\HSO_3.\\HSO_3\end{cases}$$

and was therefore the desired disulphanthraquinonic acid.

This substance, when heated with potassic hydrate to a temperature of about 180° C., becomes coloured, and when the reaction is complete the product is found to contain a sulphite and alizarin. The reaction being as follows:—

$$C_{14}H_6\begin{cases}(O_2)''\\HSO_3\\HSO_3\end{cases} + 6KHO = C_{14}H_6\begin{cases}(O_2)''\\KO\\KO\end{cases} + 2K_2SO_3 + 4H_2O.$$

Disulphanthraquinonic acid. Potassic alizarate.

The alizarin thrown down from this alkaline product is generally of a bright yellow colour, and quite as pure as the analogous precipitate obtained when dibromanthraquinone is employed.

The formation of alizarin, however, is not the primary result

of the action of potassic hydrate upon this sulpho-acid, an intermediate body being first produced. This may be called sulphoxanthraquinonic acid; its formation may be thus expressed:

$$C_{14}H_6\begin{cases}(O_2)''\\ HSO_3\\ HSO_3\end{cases} + 4KHO = C_{14}H_6\begin{cases}(O_2)''\\ KO\\ KSO_3\end{cases} + K_2SO_3 + 3H_2O.$$

Disulphanthraquinonic acid. — Potassic sulphoxanthraquinonic acid.

This substance is crystalline, and of a yellow or orange colour; it is easily soluble in water, and produce with caustic alkalies violet or blue solutions. When heated with potassic hydrate it decomposes, yielding alizarin and sulphurous acid.

We have thus the following series of bodies:—

$C_{14}H_6\begin{cases}(O_2)''\\ HSO_3\\ HSO_3\end{cases}$ Disulphanthraquinonic acid.

$C_{14}H_6\begin{cases}(O_2)''\\ HO\\ HSO_3\end{cases}$ Sulphoxanthraquinonic acid.*

$C_{14}H_6\begin{cases}(O_2)''\\ HO\\ HO\end{cases}$ Dioxanthraquinonic acid (alizarin).

I may here mention that while these experiments were in progress, M.M. Caro, Graebe and Liebermann were investigating the same reactions in Germany, and having obtained analogous results, we have agreed in future to work together on this subject.

We find that the process just described may be modified to some extent by first forming a disulpho-acid of anthracene, and then by means of oxidizing agents, converting this into the disulphanthraquinonic acid.

In the conversion of disulphoanthraquinonic acid into alizarin by the action of potassic hydrate, a peculiar reverse action takes place to a small extent, both anthraquinone and anthracene being formed. This is evidently due to a reducing action similar to that which takes place when alizarin is heated with powdered zinc, thus:—

* This substance has not been analysed as yet, but from its formation and decomposition with caustic alkalies, there can be but little doubt that the above formula represents its composition.

$$\underset{\text{Alizarin.}}{C_{14}H_8O_4} + 2HH = \underset{\text{Anthraquinone.}}{C_{14}H_8O_2} + 2H_2O.$$

$$\underset{\text{Anthraquinone.}}{C_{14}H_8O_2} + 3HH = \underset{\text{Anthracene.}}{C_{14}H_{10}} + 2H_2O.$$

The colouring matter obtained either by Graebe and Liebermann's original process or from the sulpho-acid of anthraquinone, I have invariably called *alizarin*. The identity of this substance with the alizarin of madder has however been called in question. I have therefore made some experiments upon this subject, and carefully examined these two products side by side. For this purpose I have employed both purified, sublimed, and unsublimed artificial alizarin,* and for comparison, purified sublimed alizarin prepared from madder extract.

I find that both the natural and artificial bodies crystallize in needles, which are usually curved, especially when small.

When dissolved in caustic alkali they both form violet solutions of the same tint.

When applied to mordanted fabrics, they produce exactly the same colours, bearing the treatment with soap equally. They also possess the same tinctorial value.

When dissolved in alcohol, they produce with cupric acetate, a purple solution of precisely the same shade of colour.

When examined with the spectroscope, their potassic solutions produce the same absorption bands.

Lastly, the ordinary precipitated artificial alizarin yields phthalic acid when decomposed with nitric acid.

I know of no other well-defined reaction of alizarin, and therefore judging from these, we are bound to consider artificial and natural alizarin as identical.

Artificial alizarin has been objected to as a substitute for madder, on the ground that pure alizarin will not produce madder colours, other colouring matters being required.

Now the only colouring matter in madder besides alizarin, which is not injurious to the beauty of the colours, is purpurin.

This substance differs from alizarin in many of its properties,

* To purify the sublimed artificial alizarin, it was dissolved in aqueous ammonia, and after filtration precipitated with hydrochloric acid. The precipitated colouring matter was then washed, dried, and crystallized from alcohol several times.

The unsublimed product was purified with alumina by a process similar to that described by Dr. Schunck for the separation of alizarin from madder.

for example, it dissolves in alkalies with a bright red colour, alizarin giving a beautiful violet solution under these circumstances. It dissolves in a solution of alum, forming a pink solution with a yellow fluorescence: alizarin is nearly insoluble in this menstruum. Its optical properties are also very marked, and distinct from alizarin. This is especially the case with its solution in alum, which gives two absorption bands, when viewed with the prism, in the green portion of the spectrum, alizarin giving none. Professor Stokes has shown that these differences are so distinct, that it is possible to detect purpurin and alizarin in a portion of madder not exceeding in bulk the fraction of a pin's head. Therefore, the detection of either of these colouring matters on a piece of madder print is not difficult.

Dr. Schunck remarks* that, after a long course of experiments, he has been led to the conclusion that the final result of dyeing with madder is simply the combination of alizarin with the various mordants employed, and recommends the extraction of alizarin from madder prints as the easiest method of preparing it in a state of purity on the small scale.

I have made some experiments also in this direction, and have found nothing but alizarin on finished madder prints. I could not detect purpurin even with the spectroscope.

This fact may be seen in a practical manner by removing the mordants from a madder print with hydrochloric acid, and treating the colouring matter upon the cloth with a solution of potassic hydrate. It will then be found that a blue violet solution is produced of the same shade as that given by pure alizarin. If purpurin were present in appreciable quantities, this would not be the case, as the solution would then more and more approach purple in colour, according to the percentage of this colouring matter. I do not mean to affirm that purpurin never exists on prints dyed with madder or garancin, as there are several classes of goods produced in print-works and subjected to more or less soaping, &c. Some styles of garancin work are, I believe, not soaped at all, or only slightly, the whites being cleared with dilute chloride of lime.

There can be no doubt that the higher the class of print and the more brilliant the colours, the purer is the alizarin in combination with the mordants.

I have already referred to the absorption spectra of alizarin

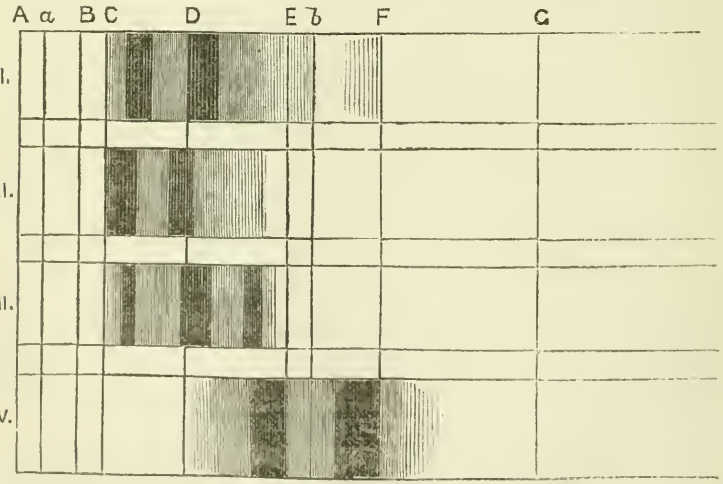
* Jour. Chem. Soc., vol. xii, p. 202.

and purpurin. There is, however, a third substance mentioned in this paper, to whose special character I must refer, as under certain circumstances it gives an absorption spectrum so like alizarin that it may easily be confounded with that body when examined with the prism. I refer to sulphoxanthraquinonic acid—

$$C_{14}H_6O_2\begin{cases}HO\\HSO_3\end{cases}.$$

It will be seen from the following woodcut that when dissolved in *alcoholic potash*, this substance gives two absorption bands in nearly the same position as alizarin when examined under like conditions. It may, however, be distinguished from this body by the examination of its solution in *aqueous* potash, this giving a *third* absorption band near to E, which although not dark is *very* distinct. Alizarin in aqueous potash produces a more general absorption, and the bands are not so sharp as when alcohol is used; a third band is also seen in this case according to Professor Stokes, but so feeble that it is almost lost in the general darkening.

In chemical properties sulphoxanthraquinonic acid differs essentially from alizarin, it being soluble in water and insoluble or nearly so in ether; alizarin behaving in an opposite manner to these solvents.



I. Alizarin in alcoholic potash.
II. Sulphoxanthraquinonic acid in alcoholic potash.
III. Sulphoxanthraquinonic acid in aqueous potash.
IV. Purpurin in sulphate of alumina.

Artificial alizarin as supplied to the dyer and printer is not chemically pure, and usually produces with alumina-mordants, colours somewhat redder than madder. It has been stated that this is due to the presence of purpurin; this, however, is not the case, as none of this colouring matter can be detected even by Professor Stokes's test; Dr. Schunck has also confirmed this.*

The shade of colour produced with artificial alizarin may be modified to some extent by regulating the temperature of the dye-bath, the colours on the alumina mordants being nearer to those produced with madder, when a low temperature is employed. The redder shade produced with this colouring matter is however often preferred, especially for Turkey red dyeing. The quality of the colouring matter appears to be under the control of the manufacturer to a considerable extent, and it is possible that eventually artificial alizarin will be prepared in a nearly chemically pure state.

A good deal has been said about anthracene, it being assumed that it cannot be obtained in large quantities. It must be remembered, however, that tar distillers have had as yet but little experience in separating this substance; but from experiments I have made upon this subject, I am led to believe that coal tar contains considerable quantities of this hydrocarbon. There can be no doubt that the kind of coal, as well as the temperature employed in the gas works, influences the quality of the coal tar as a source of anthracene, but upon these points no definite information has been obtained up to the present.

The patterns opposite the first page are dyed with artificial alizarin prepared from anthracene by the new process described in this paper.

* Of the impurities of artificial alizarin little is known as yet. Dr. Schunck has examined some residues I lately sent him, containing a considerable quantity of these bodies, and has isolated a beautiful yellow substance, crystallising in golden scales when sublimed, and not unlike rubiacin, except that it forms with alkalies a yellow instead of a red solution. This substance has no affinity for mordants.

When purifying artificial alizarin by converting it into an alumina lake, I found that upon digestion with carbonate of potash this lake gave a red-coloured solution containing a colouring matter dyeing mordants very similarly to alizarin, with this difference, that the reds were more scarlet, and the purples bluer or more slaty. I have not obtained this body in a perfectly pure state as yet, but it appears to be crystalline. It gives two faint black bands when examined in alkaline solution with the prism, but these may perhaps be due to the presence of traces of alizarin.

XVII.—*Analysis of Deep Sea Water.*

By John Hunter, M.A., F.C.S., F.R.S.E., Chemical Assistant, Queen's College, Belfast.

The present paper may be considered as a sequel to that read before the Chemical Society in December last on the analysis of sea water, performed on board H.M.S. "Porcupine." Since that time, I have examined the composition of the water taken from various depths. In consequence of the very small amounts of the samples which remained, after obtaining the quantity of the gases held in solution, and the organic matter, it was only possible to determine the more important substances contained in them, and, unfortunately, the proportion of potassium at the different depths could not be observed.

The valuable researches of Professor Forchammer on the composition of sea-water from different parts of the ocean were communicated to the Royal Society in a paper read November 17th, 1864. He procured a number of specimens from various depths in the Atlantic Ocean, between Baffin's Bay and the Equator, and found that water from the former place contained the same quantity of salts in the surface and depth; but on passing the most southern point of Greenland, the surface-water contained more salt than that from below, the difference increasing towards the Equator. In one case he found that the more dense water occurred between too weaker portions, and one of the series of analyses appended to this paper gives a similar result. He also observed that, in some cases, the amount of salt increases with the depth, and in other cases it diminishes. A number of specimens collected between lat. 50° 56′ and 50° 22′ N., and long. 12° 6′ and 15° 59′ W., off the west coast of Ireland, gave 35·613 grammes per litre of salts for the surface-water, and 35·687 for a depth of from 200 to 1,750 fathoms.

Before proceeding to mention the results of the analysis of deep sea water, I wish to direct attention to the composition of Atlantic ooze brought up by the dredge from the enormous depth of 2,435 fathoms. The portion of the ooze reserved for analysis was dried in the engine-room of the "Porcupine," in order to prevent decomposition as much as possible; when

taken out of the dredge its colour was grey, which, however, became nearly white on drying. Examined under the microscope, it is found to contain a great number of extremely small shells, apparently formed of carbonate of calcium; in addition to these, there are some siliceous forms. The principal constituents are carbonate of calcium and silica. Before analyzing the ooze, the chloride of sodium and other salts present from the evaporation of the sea-water were washed out.

Composition of Atlantic Ooze.

Depth, 2,435 fathoms; lat., 47° 38′; long., 12° 08′.

Silica	23·36
Carbonate of calcium	61·34
Alumina	5·31
Ferric oxide	5·91
Carbonate of magnesium	4·00
	99·92

The first series of analyses are of waters from the bottom and intermediate depths, commencing at 2,090 fathoms, in the immediate neighbourhood of the station at which the ooze was brought up, so that we may consider the bottom to be of the same composition in the two places. The sample from the greatest depth contains considerably more calcium than any of those succeeding, which may be accounted for by the fact of the water there being in close contact with a sea bottom containing a large amount of carbonate of calcium, while the water itself has more carbonic acid in solution than any of the superposed layers. All the intermediate depths contain about the same quantity of calcium. The magnesium and sulphuric acid are slightly in excess at the bottom, and the chlorine increases towards the surface. The bromine was about the same all through; it was determined by reducing the mixed bromide and chloride of silver by means of zinc and dilute sulphuric acid, and the results agree as well as can be expected from the very small quantity of salt at my disposal. The total amount is less in the bottom water at 2,090 fathoms than in water at 1,000 fathoms, namely, 36·324 grammes per litre in the former, and 36·473 grammes in the latter. The total amount of salts was obtained by evaporating down a small portion of the water very carefully and slowly; the heat was gradually increased, and the vessel and contents weighed several times

until the weight remained constant. It is very difficult to avoid decomposing the chloride of magnesium to some extent; but there was no other means of satisfactorily finding the total salts, as I had not enough left to enable me to separate the potassium and sodium.

The second series contain water from a much shallower part of the Atlantic. In this set we have the amount of calcium and magnesium almost constant from 862 to 100 fathoms; the sulphuric acid is slightly in excess below, and the chlorine greatest above. The salts in this case decrease from 862 to 200 fathoms—36·433 to 36·267 grammes per litre—and then increase at 100 to 36·619, while the 150 fathom water contains 36·701 grammes. A similar case was observed by Forchammer, and attributed by him to the existence of currents. The 1,270 fathoms water was from the bottom.

The concluding tables show the amount of the other elements, compared with chlorine taken as 100.

First Series.

Lat. 47° 39′. Long. 11° 33′.

Depth.	Total salts.	Calcium.	Magnesium.	Sulphuric acid.	Chlorine.	Bromine.
2090	36·324	0·8084	1·5925	3·1002	19·1820	0·3114
1750	36·478	0·5337	1·3030	2·8513	19·3547	0·4192
1500	36·462	0·5385	1·4394	2·8038	19·5659	0·3081
1250	36·399	0·5442	1·3695	2·8220	19·3905	0·4230
1000	36·473	0·5675	1·2275	2·8971	19·4695	0·4302

Second Series.

Lat. 49° 12′. Long. 12° 52′.

Depth.	Total salts.	Calcium.	Magnesium.	Sulphuric acid.	Chlorine.	Bromine.
862	36·433	0·4149	1·2887	3·1906	19.3350	0·4165
350	36·294	0·4285	1·3708	2·9307	19·2556	0·4525
300	36·395	0·4560	1·3534	3·1123	19·1927	0·4814
250	36·345	0·4885	1·3218	2·9436	19·1827	0·4218
200	36·267	0·4196	1·3534	3·0100	19·1939	0·4605
150	36·701	0·4800	1·3470	2·9619	19·3844	0·4093
100	36·618	0·4116	1·2259	2·7384	19·6770	0·3749
Lat. 50° 01′. Long. 12° 26′.						
1270	36·607	0·4720	1·3788	3·0260	19·2391	0·4742

CHLORINE = 100.

	Depth.	Total salts.	Calcium.	Magnesium.	Sulphuric acid.
First series.	2090	189·3	4·181	8·236	16·038
	1750	188·5	2·757	6·732	14·728
	1500	186·3	2·753	7·357	14·278
	1250	188·2	2·806	7·062	14·512
	1000	187·3	2·916	6·304	14·880
Second series.	862	188·4	2·145	6·659	16·501
	350	188·5	2·224	7·118	15·219
	300	189·6	2·307	7·005	16·216
	250	189·5	2·546	6·995	15·345
	200	188·9	2·186	7·051	15·671
	150	189·6	2·481	6·948	15·279
	100	186·1	2·090	6·230	13·916
	1270	190·1	2·453	7·166	15·727

XVIII.—*On the Refraction Equivalents of the Aromatic Hydrocarbons, and their Derivatives.*

By J. H. GLADSTONE, Ph.D., F.R.S.

IN Professor Landolt's important paper on Refraction Equivalents,* he shows that, assuming 5 as the value of carbon, 1·3 as that of hydrogen, and 3 as that of oxygen, we may reckon the refraction of a large number of organic compounds with a close approximation to the truth. But in the table attached to an earlier paper,† there are several refraction equivalents given which are not conformable to these theoretical values. They are the equivalents of phenylic acid, oil of bitter almonds, salicylous acid, salicylate of methyl, benzoate of methyl, and benzoate of ethyl.

In the previous papers of Mr. Dale and myself,‡ there had been given the specific refractive energies of a great variety of organic compounds, and most of these were found to be in accordance with Landolt's numbers; but the following stand out exceptionally—phenylic and cresylic acids, oil of cassia, benzol, toluol, xylol, cumol, cymol, carvol, and eugenic acid. I

* Ueber den Einfluss der atomistischen Zusammensetzung C-, H-, and O-haltiger flüssiger Verbindungen auf die Fortpflanzung des Lichtes (Pogg. Ann., cxxiii, 595).

† Ibid., cxxii, 545. ‡ Phil. Trans., 1858, p. 887; and 1863, p. 317.

have since been led to assign 4·1 or thereabouts as the value of nitrogen, and 9·9 as that of chlorine; and these throw into the list of exceptions—pyridine, picoline, lutidine, collidine, chinoline, lepidine, aniline, amyl-aniline, nitrobenzol, dinitrobenzol, chlorobenzol, and trichlorobenzol.

While investigating the essential oils, I also found salicylate of methyl, anethol, and myristicol to have remarkably high refractive indices; and similar results have since been obtained from naphthalin, benzoic acid, benzoate of potassium, sulphophenylate of potassium, chloride of benzoyl, sulphide of phenyl, chlorhydranil, and thymol. The last three substances were kindly placed at my disposal by Dr. Stenhouse.

A glance at the names of these exceptional substances will show that they consist of the aromatic hydrocarbons, with the bodies derived from or related to them; two groups of nitrogenized bases; naphthalin; and some oxidised essential oils. In the following table they are divided into these several groups:—

Substance.	Formula.	Refraction equivalent.	Calculated refraction equivalent.	Difference.
Benzol	C_6H_6	43·7	37·8	5·9
Toluol	C_7H_8	51·4	45·4	6·0
Xylol	C_8H_{10}	59·2	53·0	6·2
Cumol	C_9H_{12}	66·6	60·6	6·0
Cymol	$C_{10}H_{14}$	73·9	68·2	5·7
Chlorobenzol	C_6H_5Cl	52·1	46·4	5·7
Trichlorobenzol	$C_6H_3Cl_3$	69·7	63·6	6·1
Nitrobenzol	$C_6H_5NO_2$	56·0	47·6	8·4
Dinitrobenzol	$C_6H_4(NO_2)_2$	65·2	57·4	7·8
Aniline	C_6H_7N	51·1	43·2	7·9
Amyl-aniline	$C_6H_6(C_5H_{11})N$	91·1	81·2	9·9
Sulphide of phenyl	$(C_6H_5)_2S$	103·1	89·0	2(7·0)
Sulphophenylate of potassium	$C_6H_5KSO_4$	67·6	61·6	6·0
Chlorhydranil	$C_6H_2O_2Cl_4$	85·6	78·0	7·6
Phenylic acid (Landolt)	C_6H_6O	47·7	40·7	7·0
Ditto (Gladstone)	C_6H_6O	47·3	40·7	6·6
Cresylic acid	C_7H_8O	55·3	48·3	7·0
Benzoic acid	$C_7H_6O_2$	56·6	48·6	8·0
Benzoate of methyl	$C_7H_5(CH_3)O_2$	63·9	56·2	7·7
Benzoate of ethyl (Delffs)	$C_7H_5(C_2H_5)O_2$	71·3	63·8	7·5
Ditto (Landolt)	$C_7H_5(C_2H_5)O_2$	71·6	63·8	7·8
Benzoate of potassium	$C_7H_5KO_2$	62·6	55·4	7·2
Hydride of benzoyl	C_7H_6O	54·6	45·7	8·9
Chloride of benzoyl	C_7H_5ClO	62·2	54·3	7·9
Salicylous acid	$C_7H_6O_2$	58·9	48·6	10·3
Salicylate of methyl (Landolt)	$C_7H_5(CH_3)O_3$	68·2	59·1	9·1
Ditto (Gladstone)	$C_7H_5(CH_3)O_3$	67·3	59·1	8·2
Ditto (Delffs)	$C_7H_5(CH_3)O_3$	67·2	59·1	8·1
Hydride of cinnamyl	C_9H_8O	75·3	58·3	17·0

Substance.	Formula.	Refraction equivalent.	Calculated refraction equivalent.	Difference.
Pyridine	C_5H_5N	40·1	35·6	4·5
Picoline	C_6H_7N	47·7	43·2	4 5
Lutidine	C_7H_9N	56·1	50·8	5·3
Collidine	$C_8H_{11}N$	65·0	58·4	6·6
Chinoline	C_9H_7N	66·7	58·2	8·5
Lepidine	$C_{10}H_9N$	80·6	65·8	14·8
Naphthalin	$C_{10}H_8$	75·0	60·4	14·6
Anethol	$C_{10}H_{12}O$	81·4	68·5	12·9
Carvol	$C_{10}H_{14}O$	76·9	71·1	5·8
Thymol	$C_{10}H_{14}O$	80·2	71·1	9·1
Myristicol	$C_{10}H_{14}O$	76·8	71·1	5·7
Eugenic acid	$C_{10}H_{12}O_2$	81·1	71·4	9·7

The refraction equivalents in the fourth column are calculated from the numbers given in my paper now being printed by the Royal Society, viz., C = 5·0; H = 1·3; O = 2·9; Cl = 9·9; S = 16·0; SO_4 = 17·0; N = 4·1; NO_2 = 11·1. It will be seen that in every case they are smaller than the experimental numbers.

The first group contains every derivative of the aromatic hydrocarbons, of which the refraction equivalent has been satisfactorily determined, as far as I am aware. It will be at once seen that the hydrocarbons themselves and their chlorine substitution-products are about 6·0 above what theory requires, while the compounds from creosote are a little higher still. The azotised products, and those containing C_7, are nearly, if not quite 8·0 above the calculated values; and that peculiar compound, hydride of cinnamyl, which constitutes the bulk of oil of cassia, is well known to be among the most refractive and dispersive of bodies.

To what can this increased refraction be attributed? It is evidently connected with the nucleus of the whole group, and my first theory was that the hydrogen in benzol and its congeners or derivatives had a higher refraction equivalent than in the generality of organic bodies; in fact, that, instead of 1·3 it ought to be taken at 3·5, as in hydrochloric, hydrobromic, and hydriodic acids, or at an intermediate figure, as in nitric or sulphuric acids. Dinitrobenzol and even trichlorobenzol it is

true still exhibited the increased refraction, but the hydrogen remaining unchanged was sufficient to account for an increase of 8·8 or 6·6. It became very interesting therefore to examine some member of the same group in which less than 3 atoms of hydrogen had escaped substitution. Chlorhydranil, $C_6Cl_4O_2H_2$, appeared peculiarly well adapted to the purpose, especially as its 2 atoms of hydrogen are considered not to belong to the nucleus; and on examination of its solution in ether it was found to give a refraction equivalent of 7·6, that is about the usual amount, above the calculated value.

I am now disposed rather to regard the nucleus, phenyl C_6H_5, as an entity having an exceptionally great influence on the rays of light, and to seek an analogy in that augmentation of refractive power which certain elements (for instance, iron and phosphorus) undergo when they alter their atomicity; and this entity is not destroyed by the replacement of its hydrogen by chlorine, nitric oxide, oxygen, or sulphur. As long indeed as this nucleus retains its integrity of constitution, its special optical property continues; but when it is subjected to such chemical change as to break it up, the resulting products have only the ordinary effect on light. Thus chloropicrin $C(NO_2)Cl_3$, though prepared from trinitrophenylic acid $C_6H_3(NO_2)_3O$, has only the refraction equivalent 45·2, the calculated value being 45·8.

Thymol has claims even on chemical grounds to be considered a higher homologue of phenylic acid, and its optical character lends much support to this view. It might therefore be placed in the first group.

Of the other groups of substances having an exceptionally high refraction equivalent, I may have something to say on a future occasion.

The great dispersive power of all these bodies likewise claims a further notice.

In answer to a question by Mr. Perkin, Dr. Gladstone stated that since the above paper was sent in to the Society, he had examined the refraction of anthracene. A solution of it in benzol gave for the hydrocarbon $C_{14}H_{10}$, the value 100·3, instead of 83·0, being an excess over theory of no less than 17·3.

He had also considered more attentively the effect which an excess of carbon in the composition of a substance exerts on its propagation of light. Among the hydrocarbons, the paraffins and olefines give normal values, but all the essential oils of the $C_{10}H_{16}$ type that have been examined, more than 30 in number, give refraction equivalents a little above theory: those of the great turpentine group generally exceed the calculated number, 70·8, by amounts varying from 2 to 3, those of the orange group by amounts varying from 3 to 4.

The refraction equivalents of the typical hydrocarbons may be thus expressed in a series:—

Hydrocarbon.	Typical formula.	Refraction equivalent.
Paraffins	C_nH_{2n+2}	Normal
Olefines.....	C_nH_{2n}	„
Terpenes	C_nH_{2n-4}	„ + 3
Aromatic hydrocarbons ..	C_nH_{2n-6}	„ + 6
Naphthalin	C_nH_{2n-12}	„ + 14
Anthracene	C_nH_{2n-18}	„ + 17

These higher numbers must be considered only as rough determinations, but the gradual advance is sufficiently apparent. There is a similar advance in dispersion.

Another illustration of the increased influence on light, of carbon which is uncombined with two atoms of hydrogen or one of oxygen, may be found in a series of oxidized bodies which are obtained from various essential oils, and differ from one another only in the quantity of hydrogen.

Substance.	Formula.	Refraction equivalent.
Peppermint camphor ..	$C_{10}H_{20}O$	Normal
Bihydrate of cajeput ..	$C_{10}H_{18}O$	„
Oil of wormwood.....	$C_{10}H_{16}O$	„ + 1
Carvol	$C_{10}H_{14}O$	„ + 6
Anethol.....	$C_{10}H_{12}O$	„ + 13

Carbon alone, in the form of diamond, has only the normal refraction equivalent, 5·0

TABLE OF DATA NOT HITHERTO PUBLISHED.

Substance.	Equivalents of solvent.	Specific gravity.	Temp. centigrade.	Refractive indices.		
				A.	D.	H.
Benzol		0·887	11	1·4953	1·5052	1·5393
Ditto		0·878	10	1·4925	1·5021	1·5358
Ditto		0·886	7	1·4981	1. 5077	1·5411
Cymol		0·872	11	1·4801	1·4877	1·5130
Nitrobenzol		1·193	7	1·5438	1·5565	
Ditto		1·191	8	1·5426	1·5564	
Sulphide of phenyl		1·126	8	1·6244	1·6398	1·6942
Sulphophenylate of potassium	111·36 of water	1·092	11	1·3587	1·3638	1·3767
Chlorhydranil	23·74 of ether	0·802	12·5		1·3775	
Benzoic acid	11·14 of alcohol	0·859	7	1·3913	1·3962	1·4116
Ditto	17·44 of alcohol	0·838	8·5	1·3806	1·3850	1·3993
Benzoate of potassium	22·90 of water + 0·06 K_2O	1·139	6	1·3917	1·3974	1·4149
Ditto	38·24 of water + 0·09 K_2O	1·091	6	1·3705	1·3757	1·3904
Chloride of benzoyl		1·228	10	1·5438	1·5568	1·6012
Hydride of cinnamyl		1·059	11	1·6045	1·6253	
Naphthalin	7·95 of ether	0·789	6	1·3950	1·4005	1·4189
Anethol		0·9877	..	1·5430		1·6129
Thymol	18·39 of alcohol	0·832	8	1·3845	1·3890	1·4031
Myristicol		0·9446	..	1·4848		1·5160

XIX.—*Note on Bromopicrin.*

By Thomas Bolas and C. E. Groves.

Having occasion to prepare a considerable quantity of bromopicrin, we thought that it might be useful to state the most advantageous method, and also a few of its properties that have been hitherto undescribed.

This substance was discovered by Dr. Stenhouse in studying the action of bromine on picric acid,* but he found it better to prepare it in a manner similar to that employed for chloropicrin.

After numerous experiments we found the following to be the best process for its preparation: 4 parts of lime were slaked with 50 of water; the mixture was transferred to a glass flask; and when it was quite cold 6 parts of bromine were gradually added with constant agitation, great care being taken to prevent any rise of temperature; 1 part of picric acid was then added to the bromide of lime thus obtained, the mixture transferred to a metal vessel, and rapidly distilled. The whole of the bromopicrin was contained in the first fourth of the distillate, and after being separated from the water, was dried by chloride of calcium.

The quantity obtained by the above method varied from 46·5 to 49·5 per cent. of the bromine employed, the theoretical quantity, according to the subjoined equation, being 50·8:

$$2C_6{}^{H_3}_{(NO_2)_3}O + 44Br + 19{}^{Ca''}_{H_2}O_2 = 6C{}^{Br_3}_{NO_2} + 6Ca''CO_3 + 13Ca''Br_2 + 22H_2O$$

In order to avoid loss of bromine and to obtain a pure product at one operation, it was found necessary to use rather more picric acid and considerably more lime than the above equation indicates.

On being subjected to analysis, it gave the following results:—

I. ·5537 grm. substance gave 1·0442 bromide of silver.

* Ann. Chem. Pharm., xci, 308.

		Theory.	I.	Stenhouse.	
C	12	4·03			
Br_3	240	80·54	80·25	80·01	80·02
N	14	4·69			
O_2	32	10·74			
	298	100·00			

Bromopicrin, as is well known, is liquid at ordinary temperatures, but we find that the pure substance, when cooled, solidifies to a mass of prismatic crystals which melt at 10°·25 C. It is necessary that the bromine employed in its preparation should be free from chlorine, as otherwise the product has a lower melting point, probably owing to the presence of chloropicrin.

Although bromopicrin, as Dr. Stenhouse has pointed out, is rapidly decomposed when heated to its boiling point, we find that, under the ordinary pressure, it may be distilled without change in a vacuum.

Bromopicrin is not decomposed by cold sulphuric acid, and is a remarkably heavy liquid, having a specific gravity of 2·811 at 12°·5 C. It has also a high dispersive power, and its refractive index for the line D at 20° C. is about 1·57. It is miscible in all proportions with benzol, bisulphide of carbon, tetrachloride of carbon, chloroform, light American oil, ether, and alcohol, from the latter of which it is precipitated by water. Iodine is slightly soluble in it, giving a violet-coloured solution, and it also possesses the property of dissolving indigo in small quantity. Naphthalin is exceedingly soluble in it, especially when warm.

Tetrabromide of Carbon.

By the action of powerful brominating agents on bromopicrin, we find that tetrabromide of carbon, CBr_4, is produced, and hope shortly to lay before the Society the details of its preparation and an account of its general properties. We have apparently succeeded in obtaining the same compound CBr_4, from carbonic disulphide, and from bromoform.

XX.—*On an Acid Feed-water from the Coal Field at Stellarton, Nova Scotia, and the Results of its Use.*

By Professor How, D.C.L., University of King's College, Windsor, Nova Scotia.

In giving an account of the mineral waters of this province, I have mentioned* that a water with an acid reaction is reported to exist near Gair Loch in Picton county. The same county affords the strong brine originally described to the Chemical Society,† and also the subject of the present communication, which is made by permission of Jesse Hoyt, Esq., General Agent of the Acadia Coal Company, at whose instance my examination was conducted. While, from the nature of the circumstances under which the water is obtained, to be detailed presently, the results brought forward do not add to our scanty knowledge of the hypogene waters of the province, except as indicating the probable origin of acid waters in coal strata, they increase the number of facts recorded with regard to the chemistry of waters generally, and they especially illustrate the action of impure feed-waters on boilers, and the nature of the deposits and incrustations resulting from their use. For these reasons they may not be unacceptable to the members of this Society, as furnishing a subject for discussion.

Mr. Hoyt sent me the water for analysis because he found it was having a very injurious effect upon his boilers; he also furnished for examination the deposit and incrustation formed, his object being to find a remedy for the evils observed. I speak of *a water* because, although two waters were sent, they proved to be so far of common origin that they intercommunicated, and the considerable difference in their composition being rather in the quantity than the nature of their constituents, probably arose chiefly from dilution by surface-water or from some other temporary cause connected with the weather.

The waters were taken in December, 1869, from an artificial pond and well respectively, at the Acadia coal mines situated at Stellarton, a name chosen recently, February, 1870, by the residents as distinctive for the locality, from its furnishing the remarkable stellar-oil coal or stellarite, a mineral substance first

* Mineralogy of Nova Scotia, p. 199. † At the Meeting held Feb. 16, 1865.

described by myself,* and at the same time compared with albertite and torbanite as distinct from coals. The pond was made to communicate with the well because the latter did not furnish enough water for the boilers. The pond rests upon the measures immediately underlying the Acadia seam of coal, which is 20 feet thick, and has the reputation of being remarkably free from sulphur, as are many of the coals of this field. Communication is made with the well, which is sunk in the underlying sandstone, by means of a tunnel driven through the same rock. With this exception there is no other member of the measures in actual contact with any of the water, as the whole surface is covered with a tough red clay-drift of from five to twenty feet in thickness. The character of the water may to some extent be influenced by washings from dirt which is screened from the slack coal and piled in considerable quantities in the immediate vicinity of the pond and well. Hence it appears that the water is partly of surface origin. The water from the mine, as pumped up, is remarkably clear and is used in the neighbourhood for drinking purposes; it does not mingle with that of the pond or well, but is discharged at another point.

The water from the pond was colourless and held a little yellow flocculent matter in suspension, which was proved to contain hydrated peroxide of iron with a little organic matter and magnesia, but no carbonates. It had no odour, and no colour was given to lead paper placed in the air above the water after shaking up; its taste was chalybeate; it gave a black precipitate with sulphide of ammonium; its reaction was decidedly acid; the gas evolved on boiling did not affect baryta-water. The following were the results of quantitative analysis of the filtered water made soon after collection. The nomenclature used in my report, as more generally intelligible to practical men than any of the latest proposed, is retained:—

* Edin. N. P. Journal, and Silliman's Journal, 1860.

Contents of Pond Water in the Imperial Gallon.

	Grains in 70,000.
Sulphate of lime	8·81
Sulphate of magnesia	5·91
Sulphate of protoxide of iron	4·96
Sulphate of potash	1·53
Chloride of sodium	0·28
Chloride of potassium	0·67
Silica	0·25
Ammonia	traces
Organic matter	small
Free sulphuric acid (oil of vitriol)	1·92
	24·33
Specific gravity at 57° Fahr.	1000·299

The water increased much in acidity when boiled down; after about four-fifths had boiled away, the amount of deposit was equal to about half a grain to the gallon; the residue on evaporation, heated in a porcelain dish, became black. The sulphuric acid of the sulphates, and the comparatively large amount of iron, may have come chiefly from pyrites in the adjacent coal-dirt, and the free sulphuric acid from the subsequent alteration of protosulphate of iron.

The well-water, the actual feed-water of the boilers, was very turbid, and was constantly depositing a yellow substance, consisting of hydrated peroxide of iron, organic matter, and magnesia. Its reaction was distinctly, but not strongly acid; it had a strong chalybeate taste, and gave a black precipitate with sulphide of ammonium; it had no odour, gave more gas than that from the pond on boiling, and the gas in this case also was not carbonic acid. The results of the analyses of the filtered water soon after its collection were the following:—

Contents of Well Water in the Imperial Gallon.

	Grains in 70,000.
Sulphate of lime	25·69
Sulphate of magnesia	9·45
Sulphate of protoxide of iron	4·58
Sulphate of potash	6·44
Chloride of sodium	0·40
Chloride of potassium	0·88
Silica	0·52
Organic matter	very small
Free sulphuric acid (oil of vitriol)	0·43
	48·39
Specific gravity at 57° Fahr.	1000·891

This water deposited the whole of its iron, along with some magnesia and no doubt organic matter, on boiling down; when at about one-fifth of the original bulk, its total deposit amounted to four grains for the gallon; this deposit contained no carbonates. The difference in composition between this water and the preceding may have arisen from their intercommunication being temporarily broken by a hard frost which occurred early in December, and the dilution of the pond water during the subsequent "soft spell" in which the waters were collected. The sandstone of the tunnel and well would produce little change. It is evident that a good deal of iron has been removed, doubtless by organic matter. The free sulphuric acid has probably been partly neutralized by carbonate of lime existing in the well water itself.

At my request, Mr. Hoyt tested the waters in the pond, the well, and the boilers with litmus paper, and in each case found an acid reaction, which I considered, on observing the resulting tints of the papers returned to me, to be about equal to that I had obtained in the bottled waters as received and as evaporated.

The deposit or sediment formed in the boilers was of a bright red colour, in dry and soft cakes, up to an inch or so in thickness, apparently uniform in quality. Heated in a tube, it gave water with vapours smelling strongly of acrolein, arising from the presence of grease, introduced, of course, from the

machinery. It contained no carbonates, and only the merest trace of magnesia; a few minute black specks were observed on solution in acid. Analysis gave:—

Water and greasy organic matter	9·11
Peroxide of iron and a little alumina	54·34
Anhydrous sulphate of lime	36·55
	100·00

The incrustation formed on the boilers was described as so compact as to be removed with much difficulty. As I received it, the most solid portions were in cakes, nearly a quarter of an inch thick in parts, white and red inside, as from a mixture of peroxide of iron and sulphate of lime; some organic matter was also present. As a whole, the incrustation was a dry mass, of the colour of Turkey umber; it contained twigs and fibres of roots. Heated in a tube, it gave a good deal of water and oily white fumes, containing acrolein; carbonates were absent, and a mere trace of magnesia was found, with also a few minute black specks remaining, as above, on solution. The analytical results on selected hard portions were:—

Water and greasy organic matter	14·43
Peroxide of iron and a little alumina	13·30
Sulphate of lime (anhydrous)	72·27
	100·00

It is not surprising that, with such water as has been described, the boilers should be much injured, and that so large a quantity of iron should be found in the deposit, a quantity which indeed may be called enormous, when we find Dr. Phipson quoted as instancing a red deposit containing more than 9 per cent. of peroxide of iron as the result of the action of an impure water, such as those contaminated with metallic salts and other kinds of refuse from chemical works, and especially liable to induce corrosion.*

In addition to the simply chemical action of the sulphuric acid, originally free, and that liberated by the concentration of the Stellarton water, which would, of course, attack even homogeneous iron, and whose influence would be largely increased

* Phipson on Boiler Dposits: reviewed in Chemical News xvi, 131.

by the electrical relations of the different portions of the boiler plates, consisting no doubt of the electrically non-homogeneous portions found, as pointed out by Mr. Mallet, in wrought-iron and blister steel, there would be similar, if less injurious, results from the action of the alkaline salts classed by Professor Chandler* as electrically corroding agents. If any brass or copper should be in contact with the metal, the electrical action on the iron would, of course, be intensified. The oxide of iron is derived partly from the water itself, but principally, no doubt, as a good deal must be deposited in the well, from the decomposition of the iron salts, resulting from the action on the boiler plates. Both in the deposit and incrustation minute black specks were said to be present; these were not given in the quantitative results, as being too small in amount. They effervesced with nitric and with hydrochloric acid, but remained black, so that they no doubt contained iron and graphitic carbon; and they may have been mechanically detached from the boiler with the incrustation, or have resulted from its occasional local burning into scales, or from the local corrosion detailed by Mr. Paget in his interesting paper read before the Society of Arts, and given in abstract in the "Chemical News," xi, 219, 230, in which he dwells at some length on the electrical relations to which I have only alluded.

* Report on Water for Locomotives and Boiler Incrustations, New York, 1865.

XXI.—*On Tetrabromide of Carbon.*

By Thomas Bolas and Charles E. Groves.

Some of the combinations of bromine and carbon have been already investigated, but the tetrabromide has remained unknown up to the present time. The dibromide C_2Br_4 was obtained many years ago by Löwig* in studying the action of bromine on alcohol and ether. Völckel,† however, did not succeed in preparing it by this method. In 1862, Lennox‡ took up this subject and investigated the tetrabrominated ethylene C_2Br_4, which he obtained by the alternate action of bromine and potassic hydrate on ethylene. The tribromide C_2Br_6 is mentioned by Reboul§ as obtained from ethylene dibromide by substitution.

We will now proceed to describe the methods of preparation and some of the principal reactions of the tetrabromide, which, as already announced, we have succeeded in obtaining.

Tetrabromide of Carbon from Carbonic Disulphide.

We can fully confirm the observation made by Kolbe that bromine does not act on carbonic disulphide, when heated with it for a considerable time, at a high temperature (150°—180° C.), and the bromide does not appear to be formed even when the mixed vapours are passed through a red-hot tube.

The bromination of the bisulphide may, however, be effected by two different methods: by submitting it to the action of bromine in the presence either of bromide of iodine, or of antimony terbromide. It may be as well to mention that the bromine employed in all these experiments was free from chlorine.

Preparation.—(*a.*) 2 parts of bisulphide of carbon, 14 parts dry bromine, and 3 parts iodine were heated together in a sealed tube to a temperature of 150° C. for about 48 hours; the

* Löwig, Ann. Chem. Pharm., iii, 292.
† Völckel, Ann. Chem. Pharm., xli, 119.
‡ Lennox, Ann. Chem. Pharm., cxxii, 126.
§ Reboul, Ann. Chem. Pharm., cxxiv, 271.

contents of the tube were then washed into a flask, excess of caustic soda solution added, and the mixture distilled until no more tetrabromide of carbon came over with the water. After it had been collected, it was freed, as far as possible, from adhering moisture, dissolved in a small quantity of hot spirit, filtered, and allowed to cool, when it crystallised out in large lustrous plates. It was necessary to avoid boiling the alcoholic solution, as otherwise considerable loss occurred.

As the presence of a small portion of unaltered carbonic disulphide will cause the distillate to remain liquid after being separated from the water, it should, under these circumstances, be exposed to the air in order to allow it to evaporate, when the tretrabromide is left behind in the solid state.

(*b.*) Antimony terbromide may be substituted for bromide of iodine in the above process, employing 4 parts terbromide, 7 parts bromine, and 1 of carbonic disulphide. When the reaction was complete, the contents of the tube were treated in the same manner as when bromide of iodine was employed. The above reactions take place, although slowly, at 100° C.

Tetrabromide of Carbon from Bromopicrin.

We find that the action of brominating agents on bromopicrin, as in the case of carbonic disulphide, produces tetrabromide of carbon; but since bromopicrin itself decomposes under the influence of heat with liberation of bromine and evolution of nitrous fumes, it is advisable to conduct the operation in a flask furnished with a digestion tube, in preference to heating the materials in a sealed tube.

(*c.*) When terbromide of antimony was employed as the reagent, the following proportions were taken:—12 parts terbromide of antimony, 10 parts bromopicrin, and 8 of bromine; the reaction was generally complete in about 36 hours; but this could be readily ascertained by neutralizing a small portion of the contents of the flask, when the presence of any unaltered bromopicrin rendered itself sensible by its characteristic odour. When it was thus ascertained that the reaction was finished, the contents of the flask were neutralized and treated in a manner similar to that already described in the preparation of the tetrabromide from carbonic disulphide. The quantity obtained by this process is, however, small in proportion to the

quantity of substance employed. This is what might be expected, considering the readiness with which bromopicrin decomposes under the influence of heat. The quantity of the bromide of carbon was usually less than 40 per cent. of the bromopicrin employed.

(*d.*) Bromide of iodine may be substituted for the antimony terbromide in the above process, but its action is much less rapid.

Tetrabromide of Carbon from Bromoform.

As in the case of carbonic disulphide and bromopicrin, tetrabromide of carbon is formed by the action of the brominating agents above-mentioned on bromoform, viz., bromide of iodine and terbromide of antimony.

(*e.*) In effecting the substitution of bromine for the remaining equivalent of hydrogen in bromoform by means of bromide of iodine, the following proportions were taken :—2 parts of bromoform, 3 parts of bromine, and 1 of iodine were heated together in a sealed tube to 150°—160° C. for about 24 hours; this was occasionally opened in order to allow the escape of the hydrobromic acid formed during the reaction. When no more gas escaped on opening the tube, the contents were neutralized and distilled.

(*f.*) When antimony terbromide was employed the operation was conducted, as in the case of the bromide of iodine experiment, using 2 parts of bromoform, 2 parts bromine, and 3 of the antimony terbromide.

Analyses of Tetrabromide of Carbon.

I. ·338 grms. substance gave ·763 grms. silver bromide.
II. ·8620 grms. substance gave ·1148 grms. carbonic anhydride.
III. ·568 grms. substance gave 1·286 grms. silver bromide.
IV. ·5465 grms. substance gave 1·240 grms. silver bromide.
V. ·6487 grms. substance gave ·0860 grms. carbonic anhydride.
VI. ·519 grms. substance gave 1·173 grms. silver bromide.

		Theory.	I.	II.	III.	IV.	V.	VI.	Mean.
C ..	12	3·61	—	3·63	—	—	3·62	—	3·62
Br_4..	320	96·39	96·06	—	96·36	96·54	—	96·16	96·28
	332	100·00							

II. and III. were obtained from carbonic disulphide, I., IV., and V. from bromopicrin, and VI. from bromoform.

Carbon tetrabromide is a white substance crystallising in lustrous plates, and melting at 91° C.; that from bromopicrin, however, had a somewhat higher melting point (about 93° C.), probably arising from the presence of a minute quantity of the bromide C_2Br_6, produced by the decomposition of the bromopicrin. It has an ethereal odour somewhat resembling that of tetrachloride of carbon, and a sweetish taste.

It is almost insoluble in water, to which, however, it communicates its odour and taste. It is exceedingly soluble in ether, bisulphide of carbon, tetrachloride of carbon, chloroform, bromoform, benzol, and American oil. It is also very soluble in hot alcohol from which it is deposited in the crystalline state on cooling. When the alcoholic solution is heated it is decomposed, aldehyde being formed, and hydrobromic acid found in the solution. We endeavoured to avail ourselves of this reaction to estimate the bromine in the tetrabromide, but failed, as the decomposition appears to be incomplete, even after digestion for some time at 100° C. in a closed tube. The alcoholic solution burns with a pale green flame. Although it is acted on but slowly by cold alcohol, both alcoholic potash and soda rapidly decompose it:

$$CBr_4 + 3\left.\begin{matrix}Na\\C_2H_5\end{matrix}\right\}O + 3\left.\begin{matrix}Na\\H\end{matrix}\right\}O = 4NaBr + Na_2CO_3 + 3\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O.$$

It is unaffected at the ordinary temperature by aqueous solutions of potash and soda, and only very slowly decomposed at 100° C., but at 150° C., and upwards, the action goes on with much greater rapidity.

$$CBr_4 + 6\left.\begin{matrix}K\\H\end{matrix}\right\}O = 4KBr + K_2CO_3 + 3H_2O.$$

It is unacted on by cold sulphuric acid, but on applying heat a slight decomposition occurs, with production of an odour resembling that of phosgene. With care it can be sublimed unchanged, but when the vapour is passed through a red hot tube, a great portion is split up into its constituent elements, the carbon being deposited in the tube, and the bromine distilling over; a small quantity of a crystalline substance, however, was

obtained, whose reactions and high melting point agreed with those ascribed to the tribromide C_2Br_6 by Reboul.

Action of reducing agents on Tetrabromide of Carbon.

A saturated solution of the tetrabromide in cold alcohol was mixed with an equal volume of water, which caused the precipitation of a considerable quantity of the substance in a finely divided state; on the addition of sodium amalgam, the solid portion gradually disappeared, being replaced by an oily body. This was separated, dried, and submitted to analysis, with the following results:—

·1016 grms. substance gave ·2208 grms. silver bromide; this corresponds to 92·48 per cent. bromine; bromoform requires 94·86 per cent. bromine, and dibromide of methylene, 91·95 per cent.

		Theory.	Analysis.			Theory.
C.....	12	4·74	—	C.....	12	6·90
Br_3....	240	94·86	92·48	Br_2....	160	91·95
H	1	·60	—	H_2....	2	1·15
	253	100·00			174	100·00

From the analyses it is evident that the reducing action of the sodium amalgam first converts the tetrabromide into bromoform, and that a portion of this then undergoes a further change into methylene dibromide. In order to confirm this, a portion of the oily substance was reconverted into tetrabromide of carbon, by the action of bromide of iodine.

We have not yet investigated the action of the ammonias upon the new substance, nor the silver-salts (oxalate, cyanide, &c.), both of which promise interesting results.

XXII.—*Chemical Researches on New or Rare Cornish Minerals.*

By A. H. Church, M.A., Oxon., Professor of Chemistry, Royal Agricultural College, Cirencester.

No. 7. Restormelite.

I have obtained on various ocasions, from the Restormel Iron Mine, a mineral which might easily be mistaken for one or other

of the Chinese stones, which are grouped under the vague term agalmatolite. But on comparing the physical and chemical characters of these oriental pinites and pyrophyllites with my Cornish specimens, I found such marked differences as to induce me to make a more extended study of the subject. The material being amorphous, and evidently incompletely altered, was far from promising, but the hope of throwing some light upon the chemical history and formation of similar products, induced me to make several analyses of my specimens. The constancy of their characters and composition was distinctly proved by a physical examination, and by the experimental chemical results given below. I do not, however, think that I should be in the least degree warranted in assigning specific rank to the Restormel mineral, and though I propose for it the definite name of restormelite, its proper place appears to me that of a new variety of kaolinite. If we look at the various hydrated aluminium silicates, which have been separately recognized, we shall find that restormelite is near halloysite, but differs from that species by containing 7 per cent. of alkalies, and only half as much water; that it is not to be included under the comprehensive pinite, since that species contains only 6 instead of 12 per cent. of water; and that it is separated from pyrophyllite by the same divergence. These are chemical differences; in hardness and specific gravity further points of variation are to be observed. In fact it is only when we come to those lithomarges included by Dana under kaolinite, that we find a collocation of physical and chemical characters, nearly the same as that of restormelite. The specific gravity of restormelite is 2·58, that of lithomarge nearly the same. Its hardness is about 2, in which also it agrees with lithomarge. In its percentages of silica and alumina, its chief constituents, there is little difference, but while restormelite contains 7 per cent. of soda and potash, lithomarge contains a mere trace of these alkalies. There is less water in restormelite than in lithomarge, but as we do not know how much hygroscopic water is included in the 15 per cent. found in the latter mineral, this point is of minor importance. I think on the whole we must regard restormelite as preserving in its alkalies more evident traces of its felspathic origin than we usually find in such alteration products. I give below the analyses and characters of restormelite.

The restormelite employed for analysis was taken from

several distinct specimens. It was uniform in texture, and in colour, a faint, greenish grey, streak white, fracture subconchoidal, lustre greasy to dull. Its sp. gr. was 2·58, and its hardness 2. Heated in a tube, it readily gives off neutral water, and becomes grey and opaque. With oil of vitriol it does not gelatinize. Restormelite contains a small but variable amount of hygroscopic water, about 1 per cent. This water is lost in vacuo over oil of vitriol after some time, or very rapidly at 100°. The selected specimens for analysis were dried in the water oven, and the uniformity of the results shows the fixity of the combined water.

Analyses of Restormelite.

Analysis.	Substance taken.	Loss on Ignition.	SiO_2.	Fe_2O_3.	Al_2O_3.	$Mg_2P_2O_7$.	PtK_2Cl_6.	Na_2SO_4.
I.	1·706	·1995	—	—	—	—	—	—
II.	1·463	—	—	—	—	·0335	·139	·148
III.	·9825	·1155	—	·012	·3445	·019	·1175	·093
IV.	·842	·098	·3845	·0118	·3002	·022	—	—
V.	·914	·1065	—	—	—	—	—	—
VI.	·960	—	—	·0105	·332	—	—	—

Percentages deduced from Analysis.

	I.	II.	III.	IV.	V.	VI.
H_2O	11·69	—	11·75	11·64	11·65	—
SiO_2	—	—	[44·77]	45·66	—	—
FrO	—	—	1·11	1·25	—	·98
Al_2O_3	—	—	35·05	35·66	—	34·58
MgO	—	·92	·69	·95	—	—
K_2O	—	2·10	2·51	—	—	—
Na_2O	—	4·66	4·12	—	—	—

These results correspond pretty well with the formula of kaolinite, $Al_2O_3 2SiO_2$, 2aq., if we suppose several replacements, such as a partial replacement of hydrogen by sodium or potassium, and of aluminium by iron. Pure kaolinite would contain 46·3 p.c. silica, 39·8 p.c. alumina, 13·9 p.c. water. It would, perhaps, be more strictly exact were we to speak of restormelite as an *immature* kaolinite, rather than as a kaolinite in which subsequent changes had taken place.

No. 8.—Chalcophyllite.

In some of my previous communications to the Society, I have included the results of analyses of rare as well of new materials. Chalcophyllite, the tamarite of Brooke and Miller, the mineral sometimes termed copper-mica, is not often found in well defined crystals. I do not know of any fresh localities where this species may be procured in forms so good as in the three or four Cornish mines where it was first discovered. In consequence of the few and discordant analyses which we possess of this most beautiful mineral, I have devoted much time and labour to an endeavour to clear up the mystery of its constitution. The results to be given further on were obtained with two very choice specimens, one from Wheal Gorland, and the other from an unknown Cornish locality. I need not say that every possible care was taken to exclude all visible impurities or intruding materials from the prepared samples employed in my analyses.

It will be proper to show, in the first place, that the recorded analyses of chalcophyllite are not quite satisfactory. This will be evident enough when Chenevix found in this mineral 58 per cent. of cupric oxide and 21 of water; Hermann, 44·45 per cent. of cupric oxide, and 31·19 of water; and Damour, intermediate proportions, namely, 52·61 of cupric oxide, and 23·26 of water. Smaller variations are also to be observed in the percentage of the third chief constituent of chalcophyllite, the arsenic pentoxide. Ferric oxide, phosphorus pentoxide, and alumina, have also been detected to a trifling extent in this mineral by different analysts.

It will be readily conceived that there is some difficulty in arriving at a formula for so apparently variable a substance. The expression usually adopted has been, $8CuO,As_2O_5,12aq.$, which corresponds pretty well with the analysis by Chenevix, but in the percentage of water which it demands is quite incompatible with the results of the other analysts. All my results confirm the ratio of CuO to As_2O_5; but the accepted formula must nevertheless be modified in two particulars. I find the water present in perfectly pure and transparent crystals to amount to more than 31 per cent., while the above formula demands only 20, and I also find an amount of alumina, too

large in quantity to be neglected in constructing an expression for this species. In fact, by the results now to be laid before the Society the previous discrepancies are explained, and it will be seen that chalcophyllite is much more nearly allied to liroconite, another hydrated cupric aluminic arseniate, than is generally thought to be the case. I will here only state that the two minerals have been observed to occur together, that somewhat similar variations of colour are found in specimens of the two species, and that the oxygen ratio of their constituents is analogous, though not identical. I may also add that the alumina detected in liroconite was for some time considered an accidental impurity.

Before giving the analytical results, it should be stated that chalcophyllite cannot be dried, even *in vacuo*, without an entire change in its appearance. It then becomes opaque, paler, and of a more bluish-green, acquiring an almost pearly lustre, if in crystalline fragments. These changes correspond to a loss of 13·79 per cent. of water. At 100° C. the insignificant further loss of ·31 per cent. of water takes place. In the following analyses the finely powdered mineral was dried at 100°, and its loss of water, under these circumstances, was so constant, that it becomes impossible from this cause (as well as from other considerations) to regard any part of this water as hygroscopic. We now come to the analyses :—

Analyses of Chalcophyllite.

No.	Substance taken.	H_2O lost at 100°.	CuO.	Fe_2O_3.	Al_2O_3.	As_2S_3.	$(MgNH_4AsO_4)_2aq$.
I.	·2218	·0313	—	—	—	—	—
II.	·3325	·046	·1555	·002	·019	·0555	—
III.	·296	·042	·1347	0018	·0185	—	·076

Percentages deduced from Analyses.

Analyses.	I.	II.	III.	Mean.
H_2O lost at 100° C.	14·10	13·83	14 19	14·06
CuO	—	46·76	45·51	46·14
Al_2O_3	—	5·69	6·25	5·97
Fe_2O_3	—	·60	·61	·60
As_2O_5	—	15·49	15·58	15·54
H_2O (by difference)	—	31·46	32·05	31·75

Two formulæ suggest themselves as best expressing the above results: here are the percentages demanded by these theories, placed, for comparison, side by side, with the mean percentages furnished by analysis:—

	Theory.		Experiment.
	I.	II.	Mean.
	$8CuO,Al_2O_3,As_2O_5,24H_2O$.	$8CuO,Al_2O_3,As_2O_5,25H_2O$.	
CuO	45·39	44·82	46·14
Al_3O_3	7·35	7·26	5·97
As_2O_5	16·42	16·21	15·54
H_2O	30·84	31·71	31·75
	100·00	100·00	99·40

If we accept formula I, we shall find that a loss of $11H_2O$ out of its $24H_2O$ will correspond to a percentage loss of 14·13; with the formula II above, $11H_2O$ correspond to 13·95 per cent. Either of these numbers corresponds very closely with the actual loss of water which our mineral suffered *in vacuo*, namely, in analysis I above, 13·79 per cent., the mean result of all similar experiments being 14·06. As the residual water was determined by difference, owing to loss of arsenic on heating the mineral, I fear that the analyses will not decide between the claims of these rival formulæ, with 24 or 25 aq. As to the other constituents of chalcophyllite, the slight discrepancies between theory and experiment can be explained in a measure. The cupric oxide is a little too high, because it probably contained a trace of alumina and arsenic pentoxide, so lowering the numbers of those two compounds proportionately: part of the alumina was probably replaced by the trace of ferric oxide found. I should expect to find more ferric oxide in the grass-green specimens of the mineral than in the emerald-green ones submitted to analysis.

It now remains to be seen how the elements of chalcophyllite are arranged. The following formula corresponds to and includes most of the experimental results:—

$$\left.\begin{matrix} Cu_3(AsO_4)_2,6Aq \\ 5CuH_2O_2 \\ Al_2H_6O_6 \end{matrix}\right\} + 11H_2O.$$

If we take formula I, the expression will only differ by containing $5H_2O$ in place of the $6H_2O$, united with the arseniate.

In order to compare the formulæ of liroconite and chalcophyllite we shall have to assume the basicity of 1 of the $5H_2O$ in the latter:—

$$\left.\begin{array}{l} Cu_2H_2(AsO_4)_2 4aq. \\ 6CuH_2O_2 \\ Al_2H_6O_6 \end{array}\right\} + 11\,H_2O.$$

The oxygen ratios of basic oxide, acid oxide, and water, will then stand thus:—

Liroconite	6	:	5	:	12
Chalcophyllite ..	12	:	5	:	24

As to the general physical characters of chalcophyllite, I have only to add that the specific gravity of my specimen was 2·44; and that the pyrognostic indications usually assigned to this species require this addition, that the olive-green scales left when the crystals are heated blacken when the temperature is further raised, and finally evolve a vapour condensing to a white or straw-coloured sublimate.

XXIII.—*On the Combinations of Carbonic Anhydride with Ammonia and Water.*

By Edward Divers, M.D.

The following paper contains an account of some investigations that I have made on the chemical reactions and combinations of carbonic anhydride, ammonia, and water with each other. The properties and relations of such bodies as these being of primary importance in the theory of chemistry, they have indeed already received a large share of the attention of chemists; and therefore, besides much that has come to be known concerning them, of which it would be impossible now to ascertain the discoverers, several valuable memoirs have been written upon them. Nevertheless, I think it will be generally admitted that the combinations of these bodies are still felt not to conform in a clear manner to the ammonium theory, the theory of the general constitution of salts, and even the theory of combining proportions.

In attempting to arrive at a more satisfactory knowledge of these combinations, I have made out much that I believe will be found to be new, both to chemical literature and the traditions of the laboratory, and of service in helping to decide as to the normal character of these combinations.

General History.—The first contribution to a knowledge of the chemistry of the carbonated compounds of ammonia must be considered to be that of Black* in 1756, pointing out the difference between solution of ammonia and the solid carbonate of commerce. After this we find Priestley making out the difference between ammonia and its carbonate in his Experiments and Observations relating to Alkaline Air, in 1774.†

The first recorded quantitative analysis of a compound of carbonic anhydride and ammonia, as far as I can discover, is that by Bergmann in 1774.‡

The variable composition of the compounds of carbonic anhydride and ammonia was pointed out in 1799 by Sir Humphry Davy,§ but the results he obtained proving to be very erroneous, his statements were unreliable. The fact of the existence of different carbonates was afterwards confirmed by Berthollet, Dalton, and others.

The Ammonium Carbonates.—I. *Normal Ammonium Carbonate.*

There are certainly three combinations of ammonia and carbonic anhydride, into the formation of which water enters in sufficient relative quantity to allow of their being represented as ammonium salts of carbonic acid,—the normal, the half-acid, and the acid carbonate.

Since writing the note on the preparation and composition of the first-named of these in the Philosophical Magazine, I have ascertained several interesting particulars in the chemical conduct of this substance; so that the facts there communicated form only a small part of the history of this salt I am now able to give.

History.—The want of the normal carbonate of ammonium

* Experiments on Magnesia, Quicklime, and other Alkaline Substances. Edinburgh (1777) pp. 65, 86, 103, and 109.

† Experiments and Observations on different kinds of Air, vol. i, p. 163.

‡ Works, translated by Cullen, vol. i, p. 29. Of the Aerial Acid, Paper read in 1774.

§ Works, vol. iii, p. 47.

was only felt after Berzelius had promulgated his ammonium theory; until then the carbonate, $CO_2(NH_3)_2$, had been considered to be this body.

Berthollet* in 1806, by distilling a solution of the acid carbonate, obtained a weak solution of normal carbonate ('subcarbonate') as the distillate. But Dalton was the first to describe a solid carbonate, neutral in composition, in 1813.† He ascertained that the carbonate of commerce did not contain two atoms of ammonia to one of carbonic anhydride, and prepared a hydrated compound of these bodies in this proportion.‡

This compound contained, according to him, one atom of water, and would therefore be represented by the formula,

$$CO_2OH_2(NH_3)_2.$$

The percentage number which he gives for the ammonia is indeed very incorrect in itself; but then he determined it by using standard solution of sulphuric acid, and, as we all know, the equivalent number he adopted for ammonia is wide of the true one. But then he clearly established that in the acid carbonate the acid is only *half* saturated with ammonia, and that in the normal carbonate discovered by him the acid is *fully* saturated. He was, however, also wrong in representing the normal salt to contain, like the acid salt, but one atom of water to one atom of carbonic anhydride instead of two, as his analytical results really indicated. The following is his statement of the composition of the two salts:—

* Journal de Physique, vol. lxiv, p. 168. Troisième suite des Recherches sur les lois de l'Affinite. Extracted from the Mémoires de l'Institut de France, for 1806.

† Experiments and Observations on the Combinations of Carbonic Acid and Ammonia. Mem. of the Lit. and Phil. Soc. of Manchester (2), vol. iii, p. 18, 1819.

‡ So far as I can ascertain, he has never received credit for this, or for the real excellence of his paper, in spite of the errors it contains. Indeed Henry, in his Life of Dalton (Cavendish Society's Publications), speaks very disparagingly of this paper. The circumstances that seem to me to have contributed to this result are: (1.) The paper was published five years after it was read, in a journal which probably had a very limited coutinental circulation. (2.) The calculations of the results of his analyses are erroneous, in consequence of the atomic weight—6—he adopted for ammonia. (3.) It contains some decided errors, among which, unfortunately, is that of denying the correctness of Gay-Lussac's researches on the proportion by volume in which ammonia combines with carbonic anhydride. (4.) It was severely criticised by Thomson, in his Annals of Philosophy (vol. xv, p. 137), who, nevertheless, besides erring himself in his correction of Dalton's remarks on Gay-Lussac's researches, also mis-states another conclusion at which Dalton had arrived.

	Acid carbonate ('carbonate').	Carbonate ('subcarbonate').
Carbonic anhydride ..	58	41
Ammonia	18	25 +
Water.....	24	34
	100	100

These results show that the normal salt he examined contained two atoms of water to one of carbonic anhydride. For by accepting the percentage numbers he gives for the acid carbonate, and calculating from these the numbers for the normal salt with two atoms of water, we get just those which he gives; thus:—

Carb. A.	Am.		Carb. A.	Am.
58 :	18 × 2	::	41 :	25·4.

	Water.			Water.
58 :	24 × 2	::	41 :	33·9.

Or putting it in another way: if we apply to his numbers for the normal carbonate the correction we know to be necessary for those he found for the acid carbonate, we get almost exactly the numbers expressing the composition of the normal carbonate with two atoms of water. The calculated numbers are—

	Acid carbonate.	Norm. carb. with $2OH_2$.
Carbonic anhydride..	55·70	38·60
Ammonia	21·52	29·82
Water	22·78	31·58
	100·00	100·00

He prepared the normal carbonate in two ways, of which one was by distilling the commercial carbonate and collecting the first product of the distillation before it had been exposed to the air; and the other by adding to a warm saturated solution of the commercial carbonate sufficient ammonia to raise the proportion to the proper degree, when, on cooling, the normal carbonate was copiously precipitated.

Sir Humphry Davy obtained in 1799, a salt that seemed to be, according to him, the most ammoniacal carbonate, and by the first of the methods afterwards employed by Dalton; but he did not determine its composition.

Dr. Thomson, in the seventh edition of his System of Chemistry* (1831), stated that a normal carbonate, $CO_2OH_2(NH_3)_2$, could be formed by mixing together one volume of carbonic anhydride, two volumes of ammonia, and one volume of water-vapour. It is very doubtful, however, whether the product thus obtained is a single substance, as will be seen by the later part of the present paper.

In 1834, John Davy† repeated his brother's experiments, apparently ignorant of what in the mean time Dalton had done, and ascertained the substance obtained by Sir Humphry to be a hydrated compound of two atoms of ammonia to one of carbonic anhydride. He also confirmed the above statement of Thomson.

Hünefeld, in 1836,‡ obtained a neutral combination of ammonia and carbonic anhydride, by distilling the commercial carbonate with aqueous alcohol, but he did not determine its state of hydration.

Next, in 1839, Heinrich Rose§ also examined the most remote part of the first product of the slow distillation of the commercial carbonate, and found it to contain two atoms of ammonia to one of carbonic anhydride; but according to him there was associated with these only half an atom of water, so that it was not a true ammonium carbonate, its formula being—

$$(CO_2)_2OH_2(NH_3)_4.$$

He obtained the same compound also by distilling a mixture of sal-ammoniac and sodium carbonate.

Lastly, in opposition to the general statement to the contrary, I myself announced in a paper in the "Philosophical Magazine" for 1868,‖ that a normal ammonium carbonate having the formula

$$CO_2(OH_2)_2(NH_3)_2$$

could readily be obtained.

I have already mentioned that Berthollet obtained a solution of normal carbonate at an early date. Then, the year

* Vol ii, p. 384.

† Some Experiments and Observations on the Combinations of Carbonic Acid and Ammonia. Edin. New Philos. Journ., vol. xvi, p. 245.

‡ Journ. für prakt. Chemie., vol. vii, p. 25.

§ Pogg. Ann., vol. xlvi, p. 373. Ueber die Verbindungen des Ammoniaks mit der Kohlensaüre. Also Taylor's Scientific Memoirs, vol. ii, p. 98.

‖ Fourth series, vol. xxxvi, p. 125.

before Rose's paper appeared, Scanlan* pointed out that the action of water upon more of the commercial salt than it can dissolve, furnishes a solution containing the ammonia in much greater proportion to the carbonic anhydride than is in the commercial salt. Dalton, however, claimed to have anticipated Scanlan in this observation, and the latter admitted the justice of the claim. Rose, in his paper the year after, showed that this solution was one of the normal carbonate, with only a little acid carbonate, and gave two other methods for obtaining a solution of normal salt. One is to boil a solution of the commercial carbonate; the other is to heat the commercial carbonate very gently in a retort having its beak dipping under mercury, continuing the heat until a great part of the carbonate has volatilized and the rest become wholly liquefied, then setting aside the liquid in a closed vessel to crystallise (which it continues to do for some days), and then decanting the mother-liquor, which is a solution of normal carbonate free from acid carbonate. That a solution of the normal salt can be obtained by distilling sal-ammoniac, pearl-ash, and dilute spirit together, was known to Phillips, and perhaps others before him.

Lastly, normal ammonium carbonate, in combination with magnesium carbonate as a crystalline double salt, was prepared by Fourcroy, many years ago, and afterwards by Bucholz.†

Preparation.—Ammonium carbonate may be prepared in various ways, which all depend for their success upon either the hydration of the carbonate, the combination of ammonia and water with the acid or half-acid carbonate, or both of these actions.

(*a.*) By digesting in a closed flask the commercial carbonate, crushed small, with strong solution of ammonia for two hours, or not much less, at a temperature not exceeding 12° C., or thereabouts, the ammonium carbonate is left as a mealy, obscurely crystalline mass. It is to be dried by pressure between folds of bibulous paper; this operation, after most of the mother-liquor has been absorbed by a few changes of paper, being conducted in a chamber as small as convenient, and as far as possible filled by the salt and the paper used to dry it, every care at the same time being taken to expose it as briefly

* Reports of the British Association for 1838. Transactions of the Sections, p. 63.

† Bucholz's Gren's Grundriss der Chemie, part i, p. 275, 1809.

as possible to the free action of the atmosphere in this stage of the drying. The operation is practically complete when the salt no longer makes distinct wet marks on the drying-paper, though it will then still feel damp. If, when the drying is nearly finished, the salt is found to be firmly adhering to the paper when a change is made, the operation has been so performed as to allow of decomposition taking place, through insufficient exclusion of air, either by having adopted imperfect means for protecting the salt while it was between the folds of paper, or by having made the changes of paper too slowly or too many times. In warm weather it is well to surround the chamber with ice*.

(*b*.) By digesting the commercial carbonate (or any other carbonate of ammonium) with strong solution of ammonia in a closed vessel, at a temperature of 20°—25° until it is dissolved, and leaving the solution thus obtained in a cool place, with the vessel containing it not thoroughly closed, in order that some of the ammonia may escape, when minute crystals form, converting it at first into a semi-transparent magma, but afterwards becoming distinct, interlacing, slender prisms. One part of the commercial carbonate to four parts by weight of the strong solution of ammonia is a convenient proportion in which to take them. The digestion generally takes about two days. It may happen when the ammonia has not been allowed to escape, and the quantity of carbonate which has been added is relatively great, that a few larger crystals, having quite a different appearance to the others, will form; when this is the case, the solution must be warmed until these crystals have dissolved, and at the same time some ammonia be allowed to escape, and then on again cooling it, these crystals will not re-form. On the other hand, when by prolonged digestion at a gentle heat, a very large quantity of the commercial carbonate has been dissolved in the strongest ammonia-water, fortified occasionally by the passage of ammonia gas in the cold, the solution only yields the ammonium carbonate with difficulty, until most of the ammonia has been allowed to escape from it by keeping it

* The chamber I made use of was a small glass pan with vertical sides, having another similar pan, or else a beaker, just large enough to glide into it. On the bottom of the pan a thick layer of circular filters, just fitting the pan, were laid; then came the salt, and over this a second layer of filters, on this a pad of tow, and, lastly, the upper pan, weighted, and sometimes filled with ice.

in an imperfectly-closed vessel, and the crystals are then often large, flattened prisms. In separating minute crystals of ammonium carbonate from their mother-liquor and preparing them for analysis, the same plan is to be adopted as in the previous method. The preparation is somewhat more manageable than the preparation of the mealy form, and the presence of the crystalline lustre serves as a means of testing its success.

(*c.*) By passing ammonia through a strong solution of the commercial carbonate until it becomes charged with the gas, when crystals of the ammonium carbonate, similar to those produced by method (*b*), will form in small quantity, either while the gas is passing, if the solution be kept cool, or afterwards, on allowing the solution to stand in a closed vessel in a cool place.

(*d.*) By dissolving a sufficient quantity of the commercial carbonate in warm, dilute solution of ammonia, best in a closed or nearly closed vessel, when ammonium carbonate crystallises out on cooling. If the free ammonia be present in large quantity, the crystals are small; if it be present in very small quantity only, the salt next to be described crystallises out; while if it be present in not much more than sufficient quantity to prevent this, the crystals of ammonium carbonate are large. I have found this one of the best methods for getting large crystals.

(*e.*) By adding dilute spirit to a solution of commercial carbonate in ammonia-water, (or to any solution equivalent to this, prepared in any other way), in quantity somewhat less than enough to cause a precipitate, when the ammonium carbonate slowly crystallises out in long, flat prisms. As with the last method, the size of the crystals is generally less in proportion to the quantity of free ammonia. When strong spirit is added to a concentrated ammoniacal solution of the carbonate, the whole soon partially solidifies through the formation of minute crystals of ammonium carbonate, large prisms sometimes shooting across the mass, when the mixture is not too strong in free ammonia.

(*f.*) By dissolving ammonium carbamate in sufficient quantity in water at a gentle heat (30°—35°) in a closed vessel, when on cooling the solution and standing it aside for some time a little ammonium carbonate crystallises out.

(*g.*) By dissolving ammonium carbamate in sufficient quantity

in strong ammonia solution at the ordinary temperature, in a closed vessel, and setting the solution aside with the vessel only imperfectly closed, that ammonia may slowly escape, when ammonium carbonate crystallises out.

(*h.*) By passing carbonic anhydride into strong ammonia-water for some time, taking care to leave large excess of ammonia, and setting the solution aside in a closed vessel, when the carbonate separates in small, usually minute crystals.

(*i.*) By dissolving good commercial carbonate, crushed small, in water at a gentle heat, best in a closed, or nearly closed vessel, setting the solution aside to cool and crystallise, decanting the mother-liquor on to a fresh quantity of commercial carbonate, again effecting solution by heat, cooling, and crystallising, a second time decanting the mother-liquor, and so on, repeating these solutions and crystallisations a sufficient number of times, when, according to the extent to which the water has been treated with the commercial carbonate, either the last solution, after depositing crystals for one or two days, will, on being decanted and left for a further time in a closed vessel in a cool place, deposit large prismatic crystals of ammonium carbonate, or the solution will, in one night's crystallisation, form over the first crop of crystals a second of the ammonium carbonate, and continue for some time to yield more of this substance.* If, instead of waiting for the solution to crystallise, it be treated with ammonia-water, a precipitation of minute crystals of the salt will take place, and convert the whole into a semi-solid mass. This and method (*d*) are the best for obtaining large crystals. The crystals are relatively short and broad when this solution is allowed to crystallise slowly at medium temperatures, but when the solution which has thus been left standing for some days is exposed to the sky for a night in clear cold weather, long flat prisms generally form.

Dalton's method of producing the ammonium carbonate by the wet way has only indirectly succeeded in my hands. It is, as already described, to add to a warm saturated solution of commercial carbonate sufficient ammonia-water to make up the proportion necessary to produce a solution of the normal salt, the quantity required to be determined by experiment. What I have done is this: I have dissolved good commercial carbonate

* Details of the action of water on the commercial carbonate will be given further on. It would be inconvenient to go into them here.

of ascertained composition in one-and-a-half times its weight of hot water, in a closed bottle in a water-bath, kept at such a heat that the solution, without actual effervescence, was evolving a very slight amount of vapour of atmospheric tension; to this solution I have added the strongest commercial solution of ammonia in about the right proportion, as calculated from its specific gravity, and this has been done without the least effervescence in the ammonia-water on coming in contact with the hot solution; but I have obtained no crystals. I believe Dalton must have succeeded in getting the crystals, either by expelling some of the carbonic anhydride from the carbonate in making the solution, and thus, or in some other way, added the ammonia-water in excess, for then, as some of the methods already described show, the carbonate would probably have been deposited. I have repeated the experiment, with the view of determining this, and found that a small excess of ammonia-water had no effect, but that a considerable excess caused the formation of a few large crystals of the carbonate, the solution being kept at a low temperature.

Dalton's method by the Dry Way.—Dalton gives no further account of this method than that I have set down in the historical notice of his paper. Rose adopted, as far as description goes, just the same method as Dalton did, and obtained a compound, having only a fourth of the water in that obtained by the latter, relatively to the other constituents. I shall further on describe in detail my own experiments on the distillation of the commercial carbonate; here I wish only to point out that they are sufficient to show that there is no necessary discrepancy in the statements of these two chemists. Quite at the beginning of the distillation, long fibrous prisms form on the condensing surface. Probably these are what Dalton examined. These, I am satisfied, are the normal carbonate, though, from the difficulty of collecting them, I have not analysed them. I believe so, because similar crystals are obtained whenever ammonium carbamate or commercial carbonate is exposed to a moist atmosphere* in a closed vessel; and because they are neutral and hydrated. These crystals are not permanent, but change into acid carbonate. They are often to be seen, or the remains of their decomposition, on the sides of bottles, in which freshly

* The existence of the carbamate in the presence of moisture is supposed to be hardly a possibility, but this is a mistake, as I shall afterwards show.

prepared commercial carbonate has been recently put;* and they can generally be produced at pleasure by putting a few lumps of clean commercial carbonate in a stoppered bottle, having first slightly moistened some of them. Crystals similar in appearance are formed by slowly raising the temperature of a solution of normal carbonate either in a retort, or in a flask (with its neck sufficiently closed by a vulcanised-rubber stopper to prevent diffusion), until drops of moisture have condensed in the neck of the flask or retort, when in a short time these are converted into fibrous prisms, sometimes very long. Crystals obtained very nearly in this way were analysed by Rose with very different results in each case, but with such as inclined him to the belief that they were probably crystals of the hydrated half-acid carbonate. The following are the numbers of parts per cent. he obtained, placed side by side with the numbers calculated for the formula of the normal carbonate $CO_2(OH_2)_2(NH_3)_2$:—

	Calc.	I.	II.	III.
Carbonic anhydride ..	38·60	44·83	—	—
Ammonia	29·82	—	23·70	27·48

Allowing for change in the salt, these numbers render it probable enough that the crystals thus formed are the normal carbonate. Further evidence that they are so will be found in my analyses of the products of distilling the commercial carbonate.

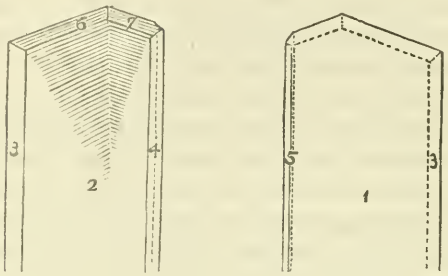
Now, if Dalton examined these crystals, he examined a different product of the distillation from that examined by Rose. Indeed, as will be seen by the records to be presently given of my own experiments, it may be said that these crystals are not a true product of the distillation, since when they are forming, the carbonate in the retort has not reached the stage of generating vapour of the pressure of the atmosphere.

Sensible Properties.—Ammonium carbonate gives out an exceedingly strong ammoniacal odour, due presumably not to itself, but to ammonia as a product of its decomposition. It has an extremely pungent taste, and at once affects the tongue as a caustic to a marked degree.

Form.—Ammonium carbonate takes the form of elongated

* It is probably the same crystals which form on the cork, or leather over the cork, closing the bottle.

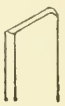
plates, or flattened prisms. Their shape is roughly indicated by the annexed cuts.



The inclination of the side-face 4 to the face 2 does not appear to be the same as that of the side-face 3; nor am I decided whether the side-face 5 is parallel or not to the side face 3; but the two faces, 4 and 5, I have found it difficult to observe satisfactorily. The faces of the crystals lose their lustre when the mother-liquor is wiped off, and the edges are rapidly destroyed. From the general inclination of the side-faces to the broad face, 2, the crystals look like half-forms, or as if the crystal had been formed with its face, 1, on the bottom of the vessel, which is indeed a common position of the crystals. The crystals have, however, the same appearance when formed with both surfaces of the plate free. The end-faces, 6, 7, are always hollowed out, and give a distinctive appearance to the crystals.

When large crystals are formed by slow growth, they are so broad in proportion to their length, that they can hardly be described as prisms. But when large crystals are produced in a single night, they are often of great length, shooting across the solution like nitre crystals. One of these I measured, and found it to be 50 mm. long, 6 mm. broad, and about 0·5 mm. thick. Crystals growing over the bottom of the vessel take the broad, short, tabular form, while those produced in the body of the solution assume the slender, flat, prismatic form. When solitary crystals are first seen suspended in the solution, they have a narrow breadth, no sensible thickness, and a considerable length relatively to their minute bulk, and are hardly, if at all, visible, except when in a position to reflect light to the eye from one or other of their broad surfaces. A very

small absolute bulk of such crystals is sufficient to convert the whole solution into a semi-transparent magma, forming as they do equally through all parts of it. When they are very minute, and in not too great quantity, the network they form can be shaken by gently jolting the vessel into a smaller bulk, retaining more or less the shape of the interior of the vessel. Shaken up on to the sides of the vessel, they form masses looking like jelly. Violently shaken up, they subside afterwards to the lower part of the vessel. When the solution filled with these crystals is left undisturbed, the crystals grow, and form a closely interlacing network of slender, apparently four-sided prisms. The ends of small crystals, whether proportionately short or not, are terminated by almost exclusively one face, the other one seen in the large broad crystals being very small, as shown in the margin. The end faces of large, long prisms are generally very imperfect, but the outline of the broad sides is most like that in the small prisms. Masses of minute crystals, such as are at first obtained by method (*b*), form, when successfully dried, soft, lustrous flakes. When proof spirit is added to a concentrated solution of the carbonate, strong in ammonia, so as to avoid immediate precipitation, minute crystals form, and soon render the fluid semi-solid; shortly afterwards, larger prisms often shoot across the semi-fluid mass. A phenomenon like the last also generally occurs when the semi-solid mass obtained by method (*b*) is cooled in ice, nitre-like prisms shooting across it. When only a very little spirit is used, short, broad prisms sometimes form at the base of the clear solution. A solution not too strong in ammonia, mixed with a suitable quantity of spirit, and left to stand in a covered vessel, becomes filled with interlacing, apparently four-sided prisms.



Chemical Composition.—In the paper in the Philosophical Magazine I gave the results of analyses of (*a*) the mealy form of the ammonium carbonate; (*b*) the minute crystals obtained from the solution formed by digesting commercial carbonate in the strongest ammonia-water till dissolved; and (*d*) crystals obtained by the action of cold on a solution of the commercial carbonate in dilute ammonia-water. To these results I can now add those of analyses of (*e* I) long, slender prisms, obtained by adding spirit to solution of commercial carbonate in ammo-

nia-water, the ammonia being determined by standard sulphuric acid in ·632 gramme; (*e* II) similar but flatter prisms obtained from the solution of the commercial carbonate in moderately dilute ammonia-water, the carbonic anhydride being determined in ·5996 gramme, and the ammonia by standard acid in ·5162 gramme; (*e* III) some prisms similar to the last, but obtained with weaker ammonia-water, the carbonic anhydride being determined in ·7989 gramme; (*h* I and II) crystals obtained by the action of carbonic anhydride gas on strong solution of ammonia, the ammonia being determined by standard acid in 1·0377 grammes, and 1·1183 grammes; (*i*) large crystals obtained by the successive action of fresh portions of commercial carbonate on water, according to the last method described of preparing the salt, the ammonia being determined by standard acid in 1·0493 grammes.

The following table exhibits these results, and the numbers calculated for the formula:—

$$CO_2(OH_2)_2(NH_3)_2.$$

	Carb. anhyd.	Amm.	
a	38·15	27·85	
b I.....	37·43	28·59	
b II	38·44	—	
b III	39·84	28·21	
d	39·15	26·50	
e I	—	26·23	
e II	38·33	28·98	
e III	39·42	—	
h I.....	—	27·85	
h II	—	27·82	
i.....	—	29·00	
			Water.
Calc.....	38·60	29·82	31·58

So many results of analyses are given in the table, in order to show the identity of various forms of the salt. It must be evident that the accuracy of the analysis of such a substance depends much more upon the success attained in preparing the sample than upon any of the other details. Therefore, as in some of the cases, the preparation of the sample for analysis was visibly more successful than in others, the results are not to be taken as of equal value in determining the composition of

the salt. Taking into consideration the mealy form of (*a*), I regard the results of its analysis as very satisfactory. Of the samples (*b*), that marked I was transferred to the weighing tube before the silky lustre of the fragments of the cake of minute crystals was much impaired, but then they were slightly damp; II and III were not dried in a closed chamber, so as to impede loss of ammonia (as in I), but only under pressure between glass plates; and III was submitted to two or perhaps three more changes of bibulous paper than II was, and in neither instance was the crystalline lustre preserved on the outside of the fragments of the cake.

Samples (*d*) and (*e* I) were dried without due care to prevent exposure to the open air as much as possible; hence they underwent considerable change before they were analysed. The same is true, but to a less extent, of samples (*h*), the object in analysing them being more to make sure as to their being the normal carbonate than to establish accurately their composition.

In sample (*i*) the size of the crystals rendered the operation of drying easier and shorter; besides this, the fact of the crystals having an appreciable thickness favourably affected the results by making of less account their surface-changes.

Behaviour on Exposure.—Ammonium carbonate gets very damp when exposed to the air. A similar change takes place in the half-acid ammonium carbonate, and has been specially pointed out by Deville. Before crystals of the ammonium carbonate can be dried they lose their lustre and become semi-opaque and moist, but retain their general shape; when pressed, they break down to a mass of wet acid carbonate. This change is not the result of absorption of moisture from the air, but of the instability of the salt in an atmosphere not charged with the products of its own decomposition. For the action goes on in a stoppered bottle until the air in the bottle is thus affected, and the salt is wet. The change may be thus represented:—

$$CO_2(OH_2)_2(NH_3)_2 = CO_2OH_2NH_3 + OH_2 + NH_3.$$

It is because of this evolution of moist gas that a feeling of dampness in the paper used to dry the salt must not be regarded as proof that some adhering moisture has not been removed from it.

Behaviour when Heated.—At about 58° ammonium carbonate is converted into water, carbonic anhydride, and ammonia, when surrounded by an atmosphere formed of products of its own decomposition. When first heated by a water-bath in a retort connected with a tube dipping under mercury, signs of decomposition are apparent in the formation in the retort-neck of drops of fluid and the fibrous crystals already described when the thermometer in the bath registers about 49° or 50°, but the progress of the change is soon arrested unless the temperature is raised, and no marked and continuous change is effected until the water-bath is at a temperature of about 59° or 60°. By maintaining the temperature of the bath at 60° no gas escapes from the apparatus, a moist, solid distillate is formed in the neck of the retort, and the contents of the retort gradually liquefy. Both the residual liquid and the solid distillate contain the ammonia in normal proportion to the carbonic anhydride, but the solid is too deficient in water, that moistening it included, to allow of its being represented as an ammonium carbonate, while the fluid in the retort is a solution of the normal carbonate, and, provided the operation is not carried too far, crystallises out on cooling. The crystals have not been analysed, but they were evidently the normal carbonate. The product of the distillation was analysed.

If the heat be carried some degrees beyond 60°, ammonia escapes during the distillation and more water rises in vapour with the other constituents. In this case the condensed salt is very moist, but still has not sufficient water to constitute it an ammonium salt of carbonic acid, and, besides, is wanting in ammonia. I shall have again to refer to these products of distillation, and will then give the numerical data of my analyses. The decomposition of the salt by heat is thus represented—

$$CO_2(OH_2)_2(NH_3)_2 = CO_2 + 2OH_2 + 2NH_3,$$

and is therefore quite distinct from that it undergoes by free exposure to the air.

Behaviour with Water.—Ammonium carbonate is soluble in its own weight of water, or slightly more, at 15°. By cooling the solution contained in a closed vessel, some of the salt crystallises out again, but mixed with other carbonates.

The saturated solution is of somewhat oily consistence. It

smells very strongly of ammonia. Exposed freely to the air it loses ammonia. Heated, it begins to effervesce between 70° and 75°, and boils freely between 75° and 80°, yielding vapours which condense into a moist solid. After boiling for awhile and then cooling the solution, it is found to be unchanged in properties, except that it is weaker.

A warm saturated solution of ammonium carbonate exhibits the phenomenon of supersaturation and sudden crystallisation in a well-marked manner when it is allowed to cool in a closed flask. If the solution does not crystallise while left at rest, it will do so suddenly on stirring it with a glass rod or pouring it out into another vessel.

Behaviour with Alcohol.—Ammonium carbonate is insoluble in alcohol. Crystals of it treated with rectified spirit are converted into acid carbonate and free ammonia. An aqueous solution of it is precipitated by alcohol, the precipitate being acid carbonate, or intermediate in composition to this and normal carbonate.

Behaviour with Ammonia-Water.—Ammonium carbonate dissolves in ammonia-water only very sparingly at a low temperature, but by digestion at ordinary temperatures, the quantity dissolved becomes greater. Strong ammonia-water, added to a concentrated solution of the carbonate, precipitates it unchanged. Ammonia gas passed into a moderately strong solution has the same effect. In cases where no precipitate is produced, the mixture will generally deposit some of the salt when cooled in ice. The small solubility of ammonium carbonate in ammonia-water is a fact which is most serviceable in preparing it. Thus nearly all the methods already given, including perhaps that in which the salt is precipitated by spirit from a weak ammoniacal solution, depend upon this influence of ammonia.

Conversion of the Carbonate into Carbamate.—But ammonia has a much more remarkable effect upon ammonium carbonate than that described in the last paragraph. By digesting crystals of the salt with water saturated at a low temperature with ammonia gas for two or more days at a temperature of 20° to 25°, they dissolve in apparently unlimited quantity, and are changed into ammonium carbamate. The mode of proceeding is similar to that adopted in method (*b*) for getting ammonium carbonate in minute crystals. Some of the strongest ammonia-water of commerce is placed in a wide-mouthed bottle, surrounded by

ice, and treated with a rapid stream of ammonia gas;* a third of its weight or more of crystals of ammonium carbonate are added, the gas still passing; then the bottle is closed with a vulcanised-rubber stopper and gently agitated for a moment, the stopper loosened to allow of restoration of atmospheric pressure by an outrush of the enclosed air, and then tightly inserted again and secured by string; the bottle is then placed where it will be exposed to a temperature of 20° to 25° and is occasionally agitated. In 30 or 40 hours the ammonia solution will have dissolved about half its weight of ammonium carbonate if so much or more has been added. In any case, though the solvent action of the liquid is not exhausted, it is well to cool the bottle again by ice and pass more ammonia gas through it, at the same time adding, if necessary, more ammonium carbonate. On opening the bottle for this purpose, after it has been cooled, the internal atmospheric pressure is found to be much less than the external pressure. The solution cooled in ice for hours gives either no crystals or only a few groups of exceedingly minute needles, which the details of the preparation of the carbonate by method (*b*) show almost certainly to be unchanged ammonium carbonate. After the addition of the salt and the ammonia gas, the operation is carried on as before. On again cooling, after 30 or 40 hours' digestion, the same appearances present themselves, but a small quantity of minute crystals is now almost certain to appear. The series of operations is to be repeated as many times as are necessary for the solution when cooled by ice, or better by exposure to the sky on a frosty night, to yield the carbamate. When this point is reached the carbamate appears in the form of beautiful large crystals and crystalline masses along with a few of the minute crystals. If the presence of the crystals be disregarded and the series of operations, including the addition of more carbonate, be again carried out, the solution after digestion yields, on cooling, a large batch of the carbamate. The other crystalline matter does not necessarily increase by repeating the operations, and when it is present in more than a very small quantity, further digestion with more ammonia suffices to make it appear in less quantity. I have thus converted carbonate of ammonium into carbamate by using only half its weight of am-

* During the passage of the gas the bottle is loosely closed by a cork, perforated to admit the gas delivery-tube, so as to diminish loss by diffusion.

monia-water, and after this had been done, there was no sign that the same solution, plus ammonia gas, would not have continued to carry on the change in any quantity more of the carbonate.

The solubility of ammonium carbonate in cold concentrated ammonia-water being slight, there can be very little of that added left unchanged. On the other hand, as the carbamate is freely soluble in ammonia-water, much of it remains in solution. No urea could be detected in the solution. The reaction is simple enough—

$$CO_2(OH_2)_2(NH_3)_2 - 2OH_2 = CO_2(NH_3)_2.$$

It may be regarded as being only an instance of the well-known influence of heat in resolving ammonium salts of polybasic acids into the ammonium salts of the amic acids, the use of the ammonia in this case being to prevent a reversion of the change. That ammonia prevents the conversion of carbamate into carbonate I shall afterwards show.

II. *Half-acid Ammonium Carbonate.*

History.—Rose first definitely obtained this salt in 1839,* but I think Hünefeld† came across crystals of it on cooling the aqueous alcohol from which he had distilled some commercial carbonate; for he described some of the crystals obtained by this cooling as rhombic plates, and as crystals of the half-acid carbonate can thus be prepared, it is probable these were some.

H. St. Claire Deville obtained it in a different way in 1852, and gave an account of its crystalline form.‡

Preparation.—The method by which the half-acid carbonate was obtained by its discoverer was that of distilling some commercial carbonate at a gentle heat in a retort, the mouth of which was joined to a tube dipping under mercury, arresting the operation as soon as the remaining contents of the retort had become entirely liquefied, and setting aside the liquid thus obtained in a closed vessel to crystallise.

The method recommended by Deville is to dissolve commercial carbonate in concentrated ammonia-water at a temperature of about 30°, and set aside the solution to crystallise with

* Poggendorff's Annalen, vol. xlvi, p. 373. Also Taylor's Scientific Memoirs, vol. ii, p 98.

† In 1836. Journ. für prakt. Chemie, vol. vii, p. 25.

‡ Comptes Rendus. vol xxxiv, p. 880. Ann de Chimie [3] vol xl, p. 87.

or without the previous addition of alcohol. It is easy to follow these directions, and yet fail in obtaining the salt, for if the strong ammonia-water of commerce be taken it will boil below 30°. If it be diluted with just sufficient water to prevent this ebullition, and then be digested for half an hour at 30° with the commercial carbonate, in a vessel nearly closed to prevent loss of ammonia by diffusion, much carbonate will not dissolve, and the solution will generally fail to crystallise on cooling, while if this solution be treated with spirit in moderate quantities, it will yield minute crystals of normal carbonate only, though as these crystals are decomposible by adding more spirit, it is possible that, could the right quantity of spirit be added at once, the half-acid salt would be precipitated. If the ammonia be taken somewhat more dilute, more commercial carbonate will dissolve, and on cooling the solution crystals will form in it, but still of the normal carbonate—long, more or less flattened prisms; the addition of spirit in moderate quantities will be followed by the formation of similar crystals,* while spirit in large quantity will solidify it. If during the digestion at 30° the mouth of the vessel be only very imperfectly closed, or if ammonia more dilute be taken, and enough commercial salt be used, the solution on cooling will yield the half-acid carbonate in the form of extremely thin plates, if it be put in too cold a place, or of larger and thicker plates if the solution be of the right strength, and be left in a place of medium temperature. Such a solution will also yield the half-acid carbonate in thin plates after addition of spirit in moderate quantity. The half-acid carbonate is also formed when potassium carbonate, its equivalent of sal-ammoniac, and ordinary rectified spirit mixed with about half its weight of water are distilled together, and the first portions of the distillate collected apart. Crystallisation of this distillate soon occurs, the crystals being at first normal carbonate, I think, or normal carbonate mixed with the half-acid salt; but slowly most of the crystalline matter becomes evidently half-acid carbonate. I have not analysed these crystals, but I have no doubt of their nature from their appearance; and besides, the circumstances of their formation are just those adapted to cause the production of this salt.

To the methods given by Rose and Deville I have to add

* Analyses of these crystals have already been given (p. 134, c. I, II, III), in the table of analyses of the normal carbonate.

two others quite different. The first and most important one is the last method given for preparing the normal carbonate. A concentrated solution of commercial carbonate in warm water is made in a loosely-closed vessel, and left to crystallise; the operation is repeated again and again with the mother-liquor and more of the carbonate of commerce, until in place of the compact crop of crystals at first obtained, a bulky and loosely arranged crop of thin plates is produced; this and those succeeding it are crops of the half-acid carbonate.*

By using not too great a charge of commercial carbonate, and allowing the crystallisation to go on, in a place not too cold, crystals form and grow slowly to a considerable size; or large crystals may generally be obtained by decanting the mother-liquor, after twenty-four hours' standing, off the first or second crop of half-acid carbonate, and leaving it undisturbed in a closed vessel for some weeks.

A modification of this method is to heat some commercial carbonate in a retort with just enough water to cover it, at a temperature not exceeding 60°, until all is dissolved, then cooling the solution, and setting it aside to crystallise, when it yields the half-acid carbonate mixed with acid carbonate.

Pelouze and Frémy state, in their "Traité de Chimie,"† that the half-acid carbonate, identical with that obtained by Rose, may be procured by cooling a solution of commercial carbonate to about 0°, and this statement re-appears in one of our standard English works on Chemistry. It is utterly at variance with my own experiments on the subject. When the solution has been strong enough to crystallise, the crystals obtained at 0° have always proved to be the acid carbonate. And further, if a solution which has deposited crystals at 0° is heated up with more of the commercial carbonate, and again cooled, the crystals which form are still those of the acid carbonate. Pelouze and Frémy are besides in this statement in direct opposition to H. St. Clair Deville, who, in his paper, "Sur la Forme et la Composition des Carbonates Ammoniacaux,"‡ says that prismatic flattened crystals of the acid carbonate are produced by greatly cooling a solution of the commercial carbonate.

The other new process is the distillation of the ammonio-

* See note, p. 179.

† Vol. ii, p. 483.

‡ Ann. de Chimie [3], vol. xl, p. 87.

magnesian carbonate, the products being a fluid distillate, giving crystals of the half-acid carbonate, and a solid directly deposited in the neck of the retort of which the more remote parts are also this carbonate. Further details of the distillation will be afterwards given.

To ensure success in preparing the half-acid carbonate for analysis, similar precautions to those recommended for preparing the normal carbonate should be taken, and, as in the case of this salt, when the crystals are small a feeling of dampness in the drying-paper must be disregarded, and the operation arrested as soon as the crystals cease to make wet spots on bibulous paper pressed against them for a few moments.

Sensible Properties.—Half-acid ammonium carbonate has a very pungent ammoniacal taste and smell, but the pungency is less intense and persistent than that of the normal carbonate.

Form.—It occurs in the form of thin, elongated, six-sided plates, or when these plates are left to grow in their mother-liquor, of flattened, right rectangular prisms terminated by the faces of a rhombic octohedron.

Measurements of the angles of the crystals are given in Deville's paper in the "Annales de Chimie."

Chemical Composition.—Results of the analyses of the half-acid carbonate have been published by Rose and Deville in their respective memoirs already referred to. Rose deduced from his analysis the formula—

$$(CO_2)_3(OH_2)_5(NH_3)_4,$$

and Deville has adopted the same formula. My own experiments have led me to adopt a different formula. The details of my analyses are as follows:—

(I *a*.) Of the salt in fine, good-sized crystals obtained by the action of water on successive quantities of the commercial carbonate, apparently well-dried, and with lustre unimpaired, 1·0055 grms. neutralized a volume of standard sulphuric acid equivalent to ·2474 grm. of ammonia.

(I *b*.) 1·1348 grms. of the same neutralized a volume of standard sulphuric acid equivalent to ·2754 grm. of ammonia.

(I *c*.) 1·0616 grms. yielded with hydrochloric acid ·5209 grm. of carbonic anhydride to soda-lime.

(II *a*, and *b*.) Two samples of crystals obtained in a similar way in another experiment were employed, the one for the

determination of the ammonia by standard sulphuric acid, and the other for the determination of the carbonic anhydride by the method followed above.

(III *a*, and *b*.) Two other samples from the same batch of crystals as the last, but dried separately, were used to determine, as before, the ammonia and the carbonic anhydride. The numerical details of these analyses and of (II *a*, and *b*,) are unfortunately lost, but the quantity employed in each case was about one gramme.

(IV.) Of crystals deposited by the fluid distillate yielded by the ammonio-magnesian carbonate, 1·1288 grms. gave, with hydrochloric acid, ·5457 grm. of carbonic anhydride to soda-lime, and ·8568 grm. of ammonium chloride = ·2725 grm. of ammonia.

(V.) 1·1266 grms. of the more remote part of the solid deposit in the neck of the retort, obtained by distilling ammonio-magnesian carbonate, gave ·5466 grm. of carbonic anhydride, and ·8809 grm. of ammonium chloride = ·2802 grm. of ammonia.

The percentage numbers of these analyses, together with the numbers calculated for a salt having the formula—

$$(CO_2)_3(OH_2)_4(NH_3)_4$$

are given in the annexed table.

	Carb. Anhy.	Amm.	
I *a*	—	24·60	
I *b*	—	24·27	
I *c*	49·07	—	
II *a*	—	24·17	
II *b*	48·19	—	
III *a*	—	24·14	
III *b*	48·62	—	
IV	48·34	24·14	
V	48·52	24·87	
			Water.
Calc.	48·53	25·00	26·47

The calculated numbers for a salt having the formula

$$(CO_2)_3(OH_2)_5(NH_3)_4$$

are—

Carbonic anhydride	45·52
Ammonia	23·45
Water.....	31·03
	100·00

so that the results of my analyses point unmistakeably to the formula having four atoms of water. It must be taken into consideration that in no case can the samples analysed be quite dry, as the decomposition by which ammonia is liberated also sets free water; because the presence of this water must lower the numbers found for both the carbonic anhydride and the ammonia, thus making the numbers for the former correspond closely to the calculated number, in spite of the decomposition which the salt has undergone, and those for the latter show a greater deviation from the calculated number than the actual loss of the ammonia itself would cause.

The results of Rose's analyses correspond closely with the numbers calculated for a salt containing five atoms of water:—

Rose's Analyses.

	I.	II.	III.	IV.
Carbonic anhydride ..	—	45·35	44·61	44·69
Ammonia	23·69	—	—	—

As I have already said, when speaking of the normal carbonate, the accuracy of the results of an analysis of such changeable salts depends very much upon the success in preparing them for analysis. Rose makes no mention of the method he adopted for getting the salt in the dry state undecomposed, or of his success in doing so; yet it will be seen, on examining his results, that the ammonia is slightly in excess of, while the carbonic anhydride is actually less than, the calculated quantity—a somewhat anomalous result, admitting the accuracy of his analyses.

If it be assumed that the salt analysed, which was in very thin plates, retained some of the mother-liquor, this difficulty respecting the results will be removed; for the mother-liquor from the crystals was itself a solution of *normal* carbonate, according to Rose. This assumption we are justified in making; for it has been shown by Deville's results that other analyses recorded in Rose's paper prove that the crystals employed must have contained mother-liquor in their interstices. And in further support of this assumption, we have also Deville's testimony, that the half-acid carbonate can hardly be obtained at once dry and undecomposed.

Turning now to Deville's deduction of the same formula as

Rose's, from the results he himself obtained, we shall not find it, I think, more satisfactory than that of the German chemist. He gives the annexed table of his analyses, the samples—none of them dry—being drier in the order of their numbers. (The water was determined directly.)

Deville's Analyses.

	I.	II.	III.	IV.	Mean.
Carbonic anhydride ..	41·4	46·8	46·6	47·8	45·65
Ammonia	21·1	23·7	24·2	23·6	23·15
Water	37·5	29·5	29·2	28·6	31·20

The practical accuracy of these analyses, as such, cannot be impugned; they were performed with great precaution to avoid sources of error, and the three constituents were all determined by a single operation in each case. Now, their mean results correspond closely enough with the percentage numbers for the five-atoms-of-water formula. But then we are certainly not right in taking these mean results as a true indication of the composition of the salt. We can only properly take the mean results of a series of analyses as likely to be more accurate than the results of a single analysis, after we have satisfied ourselves that the unavoidable and undetected imperfections in the performance of the operations are as likely to have influenced each result in one direction as in the opposite. With the present series of analyses, we know this not to have been the case; but that, on the contrary, every sample used contained adhering water, and one more than another; and further, that every sample might have lost ammonia, while none could have had it in excess. Obviously, therefore, it has been wrong to take, as has been done, the mean percentage quantities of the constituents as the nearest approach to the quantities in the pure salt.

I shall now endeavour to show that the several results obtained unequivocally indicate, when taken in conjunction with each other, that the salt examined was a half-acid carbonate, having *less than five* atoms of water. All the samples, save the last, show but very slight evidence of loss of ammonia, and even in this the ammonia need only to have been 24·6 instead of 23·6 to be in the right proportion to the carbonic anhydride. All the samples were damp; but as the first sample yielded

8 per cent. more water on analysis than the second and third samples, equally free from decomposition, but better dried, no other conclusion can be come to than that either the first sample was a very wet one indeed, or else that a more hydrated half-acid carbonate breaks up, while in a moist state, into water and a less hydrated one—which no one contends for, and which, from the facts of my own analyses, I cannot admit. In the second and third samples, the water is nearly 2 per cent. less than the calculated quantity for five atoms; and yet both had practically suffered no decomposition, and both were damp. How is it possible, therefore, from these results, to deduce for the salt the formula with five atoms of water? In the fourth sample, the water is even $2\frac{1}{2}$ per cent. less than the calculated quantity; but then this sample was somewhat decomposed. It is not too much to suppose that, as the first sample contained 8 per cent. more water than the others, these, moist as they were, still retained $2\frac{1}{2}$ per cent. of moisture. And I contend that, had the drying been carried on uninterruptedly, instead of in four stages, as was done, and with due protection of the salt from the free action of the air, more water might have been absorbed from the wet salt, without such a loss of ammonia as would have rendered the indication of the analytical results ambiguous. Even, however, as they stand, the results indicate the salt with four atoms, in a slightly decomposed and moist state; and in this state they are described to have been. They contain, in this moist state, only $2\frac{1}{2}$ per cent. too much water for this formula. I consider, therefore, that Deville's analyses in reality require the adoption of the formula with which my own analyses so closely agree.

It may be added that, when considering the relations and analogies of this salt, a fifth atom of water is found to render its composition peculiar, if not abnormal.

Chemical Behaviour.—I have little to say of the behaviour of the half-acid carbonate under circumstances capable of affecting it. The change it undergoes into acid carbonate, when exposed to the air, is quite analogous to that undergone by the normal carbonate:—

$$(CO_2)_3(OH_2)_4(NH_3)_4 = 3CO_2OH_2NH_3 + OH_2 + NH_3.$$

It is the difficulty of preventing this change, which renders

so very doubtful the accuracy of Rose's analyses.* When heated, its crystals melt, and are decomposed. It is soluble in a little more than five parts of water at 15°; less water than this first becomes saturated, and then slowly decomposes the undissolved salt, leaving behind acid carbonate. Its solubility is, therefore, as nearly as can be stated, that of the acid carbonate it may be said to contain; 272 parts containing 158 parts of the acid carbonate, or about three-fifths of their weight. For the acid carbonate is soluble in 8 parts of water, and, therefore, three-fifths of a part in about 5 parts. A solution saturated at 20° evolves sufficient carbonic anhydride to repel the stopper of a bottle containing it; and, gently heated, effervesces copiously. A saturated solution, cooled, gives good crystals of acid carbonate. It is also decomposed by spirit, acid carbonate being left undissolved. Ammonia has, no doubt, an action upon it, compounded of its respective actions upon the normal and acid carbonates. In short, the half-acid carbonate seems to be intermediate in its other chemical properties, as it is in composition, to these carbonates.

When the half-acid carbonate is obtained by treatment of the commercial carbonate with water, the mother-liquor from the crystals is equivalent in composition to a solution of normal carbonate, with or without a slight excess of ammonia. And Rose also found that the mother-liquor from the crystals formed by his method was a solution of normal carbonate. From this somewhat remarkable fact the half-acid carbonate seems to be totally insoluble in a concentrated solution of normal carbonate. An explanation of this fact on another assumption will, however, be given in another part of this paper.†

I may here mention one fact of interest concerning crystals of the half-acid and normal salts, viz., that they appear to act on the glass, both English and German, of the bottles and flasks in which they are stored for some time, destroying the transparency of its surface. I have not observed the solutions of these salts to do so.

* On allowing the crystals of half-acid carbonate to decompose in a limited quantity of air, Deville has observed crystals of acid carbonate form, which he thinks belong to a different system from that of the ordinary crystals of acid carbonate.—Comptes Rendus, vol. xxxiv, p. 880. See, however, p. 202.

† Page 214.

III. *Acid Ammonium Carbonate.*

History.—Berthollet announced his discovery of the acid carbonate in 1806, in his *Troisième Suite des Recherches sur les Lois de l'Affinité*,* and gave an excellent account of its properties. Whether he was really the first to recognise the existence of this salt I cannot say. He obtained it in the crystalline condition. Schrader was one of the first to examine the acid carbonate after Berthollet; I have not had an opportunity of consulting his paper.

Dalton in his paper in 1813 gives an account of his investigation of the formation of this salt by exposure of the commercial carbonate to the air; and analysed and described it.

Phillips described a new form of it in 1821.† Rose, in his paper on the Carbonates of Ammonia, asserted the existence of acid carbonates of different degrees of hydration.

The angles of the crystals have been measured by Gustave Rose,‡ Hallows Miller,§ and H. St. Claire Deville.‖

Preparation.—(*a.*) By exposing the commercial carbonate, the half-acid carbonate, or the normal carbonate, to the air, when the acid carbonate is left in the mealy condition.

(*b.*) Also by exposing ammonium carbamate to the air, when a little of the acid carbonate is formed and left behind in the mealy condition.

(*c.*) By treating the commercial carbonate, or the half-acid carbonate, with insufficient water to dissolve it, when the acid carbonate is left in the mealy condition. By treating similarly the normal carbonate a very little acid carbonate seems also to be formed.

(*d.*) By treating the commercial carbonate, half-acid carbonate, or normal carbonate with aqueous alcohol, when the acid carbonate is left in the mealy condition.

(*e.*) By forming a sufficiently strong solution in water of the commercial carbonate, or the half-acid carbonate, and then

* Journal de Physique, vol. lxiv, p. 168. (Extrait des Mémoires de l'Institut de France.)

† Annals of Philosophy, vol. xvii, p. 110.

‡ Poggendorff's Annalen, vol. xlvi, p. 373, in his brother's paper, Ueber die Verbindungen des Ammoniaks mit der Kohlensaüre.

§ Transactions of the Cambridge Philosophical Society, vol. iii, p. 365.

‖ Annales de Chimie [3], vol. xl, p. 87.

reducing the temperature, when the acid carbonate crystallises out.

(*f.*) By adding alcohol to an aqueous solution of the commercial carbonate, the half-acid carbonate, or the normal carbonate, when the acid carbonate deposits in crystals.

(*g.*) By treating an aqueous solution of the commercial carbonate, the half-acid carbonate, or the normal carbonate, with carbonic anhydride, when the acid carbonate crystallises out.

(*h.*) By mixing together carbonic anhydride, ammonia gas, and water-vapour, in atomic proportions, when it is deposited (Thomson). The action of carbonic anhydride in excess on an aqueous solution of ammonia has a similar result. But in both these cases I consider there is sufficient evidence to show that the acid carbonate is in reality formed by the action of carbonic anhydride and water on ammonium carbamate first formed. This evidence I shall give presently.

A modification of Thomson's method is to condense the vapours produced by heating some acid carbonate itself. The details of the method are as follows:—Some acid ammonium carbonate in crystals, crushed small, and dried by exposure to the open air, or, better still, over oil of vitriol, is passed into a dry retort with a sufficiently long neck, or with its neck prolonged by a glass tube, which is better. The retort is placed in a water-bath with its mouth, or the open end of the tube prolonging the neck, as the case may be, dipping under mercury. The heat of the water-bath is then brought to the temperature of 62° C., and not allowed to pass this. After a while no gas or air escapes through the mercury, if the heat be properly regulated; so that this fact serves, as well as the height of the thermometer, to indicate when the heat is getting too high. If the heat be allowed to fall too much, the mercury rises in the tube. At first, liquid drops form on the neck of the retort, which gradually solidify into needle-like crystals. These again lose, more or less, their transparency; and then the process of formation of the deposit can no longer be followed. The acid carbonate forms in bulk at a distance of about 16 to 20 centimètres along the neck from the body of the retort. The operation is a very slow one. When it is arrested the neck of the retort is cut off and broken up, the product chipped off from the fragments, and its purity ascertained by leaving it exposed for a time in dry air, when if pure it will retain the translucency it

possesses. The outermost layer and some other parts of it will be sure to prove impure. If the acid carbonate is more rapidly converted into vapour, the process fails. When successfully carried on, if the process be arrested at any time, and the contents of the body of the retort examined, they will be found to be dry, unchanged acid carbonate, having only an evanescent odour of ammonia. In the other case the contents of the retort will be damp or wet, and much more ammoniacal.

Sensible Qualities.—Acid carbonate has a cooling, saline taste, free from ammoniacal character until it has been retained in the mouth for a short time. It has no smell when dry; when damp it smells of ammonia.

Form.—It occurs in the form of powder; in crystals, transparent or opalescent, obtained from water; and in crystalline semi-transparent cakes.

Crystalline Form.—A great deal has been written on this subject. The crystals belong to the right prismatic system, and exhibit the faces of the three orders of rhombic prisms, as well as the three pairs of faces of the right rectangular prism. When the crystals form in a solution of commercial carbonate, cooled a little below its point of saturation; or in a not too-concentrated solution, prepared by Rose's method, so generally described in the text-books, of pouring hot water over the carbonate in a flask and then corking the flask; or in a solution of commercial carbonate, moderately strong, which has been treated with a stream of carbonic anhydride, they are hard and brilliant, and have the general contour of a flattened ovoid. The flatness of the crystals varies according to circumstances, and depends upon the relative development of the brachy- and macro-pinacoids of the rectangular prism. The principal circumstance affecting this development appears to be the strength of the solution in the more basic carbonates of ammonium. Generally there are to be seen among the ovoid crystals deposited from a cooled, saturated solution of commercial carbonate, some long, essentially four-sided crystals with truncated summits. Their form is due to the fact that the faces of the rhombic prism of the first order, and the basal pinacoids of the rectangular prism, are those principally developed. They do not differ in composition, or otherwise in form, from the first-described crystals. They give way to, or else are transformed into, the other variety when left for a time in their mother-

liquor. When a warm saturated solution of acid carbonate is made by digesting the acid carbonate with the water in a firmly-closed bottle, the crystals which form are opaque, and first appear as simple rhombic prisms with dihedral summits. (The brachy-pinacoids of the rectangular prism are also visible.) These, however, rapidly thicken, and then might be described as octahedrons on a rectangular base. They have the same faces as the previously-mentioned forms. They readily cleave into long rhombic prisms. Their opacity is evidently due to their having a composite structure and retaining mother-liquor in their interstices. When a very concentrated solution of the commercial carbonate is made in warm water in a flask, and especially when some effervescence is allowed to go on, and the solution allowed to cool, crystals, very different in appearance from those already described, make their appearance. They generally form at the surface of the solution, and remain hanging vertically; and present a remarkable appearance from being closely packed together, and all extending down into the solution to an equal depth, with their lower edges parallel to the surface of the solution. In other cases these crystals form at the bottom of the vessel, and this generally happens when the crystals are prepared by taking a solution of commercial carbonate which has already yielded a good crop of crystals, and dissolving in it, by the aid of heat, as much, or nearly as much, fresh commercial carbonate as possible. When the crystals form at the bottom of the vessel, some rest on their broad sides, but most of them stand up, closely packed in groups, nearly parallelly arranged, with their angles, not their edges, projecting upwards.

They have not the transparency and brilliancy of the ovoid crystals, but this is evidently due to the peculiar character of their faces, and not to the existence of any interstices in them. They have the form of thin, rectangular, and nearly equilateral plates, with or without the corners slightly cut off, with their broad faces crinkled and with bevelled edges. The faces forming the edges and truncated corners of the plates, are those of the different orders of rhombic prisms apparent in the previously-described crystals. The broad faces of the plates are not at all like true crystalline faces. They are not only crinkled or waved, but are not always in their general bearings parallel to each other and to the normal macro-pinacoids of the rectangular

prism, the places of which they occupy. Looking at the separate plates, these faces would probably be taken to have been produced by the contact of one crystal with another, or with the surface of the vessel; but this is not the case. In the nearly parallel groupings of crystals, already described, the plates are distinctly out of contact with each other, except just at the base from which they spring in common. They are identical in composition with the other crystals. According to Deville, the angles of these crystals measure the same as those of the others.

These are the only forms I have seen. Rose has, however, described crystals, also right rhombic prisms, which have different angular measurements, identical with those of the corresponding potassium-salt. These, however, he only succeeded in obtaining once. Deville, in his paper, "Sur la Forme et la Composition des Carbonates Ammoniacaux," read before the French Academy in 1852,* does not admit the existence of this second form of right rhombic prism, but thinks that he has seen oblique rhombic prisms of acid carbonate produced by the decomposition of the half-acid carbonate. But in his paper on the same subject, in 1854, in the "Annales de Chimie,"† attributing little weight to his previous observation of what appeared to be a second crystalline form of the acid carbonate, he states that his study of the crystalline form leads him to conclude that only one acid carbonate exists, and points out that as its known form is not isomorphous with that of the corresponding potassium carbonate, both these salts will perhaps be found one day to be dimorphous; evidently implying that the unknown form of the one carbonate will prove to be the isomorph of the known form of the other. Should this suggestion of Deville's prove to be the case, the correctness will be established of Rose's observation of crystals of the ammonium salt isomorphous with the potassium salt, which though discredited by the first-named chemist has not been disproved by him.

The cakes of acid carbonate produced by its slow distillation, exactly resemble well-crystallised specimens of the commercial carbonate. They are translucent, and, in thin pieces placed in water, almost transparent. They are formed of columnar crystals perpendicular to the surfaces of deposition, the crystals

* Comptes Rendus, vol. xxxiv, p. 880. † S. 3, vol. xl, p. 87.

being apparently right rhombic prisms. This form of the acid carbonate sometimes occurs in commerce associated with the ordinary commercial carbonate, as will be afterwards more particularly pointed out.

Chemical Composition.—Rose analysed the acid carbonate prepared in different ways, and obtained results which led him to consider that the following acid carbonates existed:—

$$CO_2OH_2NH_3$$
$$(CO_2)_4(OH_2)_5(NH_3)_4$$
$$(CO_2)_2(OH_2)_3(NH_3)_2.$$

Before Rose carried out his investigations, John Davy had examined the acid carbonate produced in four different ways, and found its composition uniform; one of these ways being that in which Rose prepared the acid carbonate found by him to have the composition indicated by the second of the above formulæ. H. St. Claire Deville has more recently examined the acid carbonate obtained in various ways (including that which yielded the crystals to which Rose gave the second formula), and he has found that it always has the same composition. The crystals obtained by passing carbonic anhydride into a solution of commercial carbonate, are identical in form and appearance with those obtained by pouring hot water on commercial carbonate, which, according to Rose, have the second formula; and they have the composition indicated by the first formula, according to Berthollet, J. Davy, Deville, &c. The existence, however, of an acid carbonate having the composition indicated by the second formula is admitted in the latest edition of one of our best English text-books.

The salt found by Rose to have the composition represented by the third formula, was a product of distillation once only obtained by him in small quantity. For this reason, and from a consideration and repetition of some of Rose's methods of preparing carbonates by distillation, I am disposed to regard the existence of such a salt as extremely doubtful.

I have repeatedly analysed the acid carbonate prepared in various ways, and have always obtained results very closely in accordance with those answering to the composition of one atom each of carbonic anhydride, water, and ammonia—with one exception. This occurred in the case of the opaque crystals obtained by cooling a warm aqueous solution of the acid car-

bonate. A sample of the crystals yielded only 54·9, instead of 55·7 per cent. of carbonic anhydride. But on taking another sample, and crushing the crystals into very small fragments, and thoroughly pressing them in paper, they yielded, on analysis, 55·57 per cent.: after drying, the lustre of the faces of the crystals was unimpaired, so that the water removed was not formed through efflorescence of the crystals. It is unnecessary to give the details and results of the other analyses of this salt.

Behaviour on Exposure.—It is probably quite fixed in dry air. In ordinary air it is very slowly dissipated, as was pointed out by Dalton. According to John Davy, it is decomposed by the atmospheric moisture, and rendered alkaline. Certainly, the moister it is, the more ammoniacal it renders the air confined with it in a bottle. By exposure to air, the faces of the crystals lose much of their lustre. It is not quite easy to recognise the nature of the change which the salt undergoes by exposure; for example, when the salt has been left for a while in a closed bottle, how is the strong smell of ammonia which is generated to be accounted for? What has become of the carbonic anhydride that was in combination with it?

Behaviour when Heated.—Like the normal carbonate, when heated in a retort, a little of it is first decomposed, and yields a few drops of liquid distillate, at about 49° C., which gradually crystallise in needles; while the rest, getting thus enveloped in an atmosphere of the products of this decomposition, undergoes no change at this heat. At about 60° it is slowly decomposed into carbonic anhydride, water, and ammonia. As I have already described, these three substances re-form the acid carbonate in the cool part of the retort, and the salt in the retort remains dry. When the heat is carried much above 60° C., the salt remaining in the retort gets wet, a moist solid, having no longer the composition of the acid carbonate, forms in the cool part of the retort-neck, and carbonic anhydride escapes. The nature of this solid distillate will be considered along with that of the products obtained by distilling the normal carbonate, and of other products of distillation. The effect of heat is therefore thus represented:—

$$CO_2OH_2NH_3 = CO_2 + OH_2 + NH_3.$$

Behaviour with Water.—As was first pointed out by Berthollet,

the acid carbonate dissolves in about 8 parts of water, at 15° C. By exposure to the air this solution rapidly loses carbonic anhydride, but, as also pointed out by Berthollet, this loss is soon arrested. Gently heated, it effervesces. The solution placed in contact with solid acid carbonate decomposes it even at low temperatures, large bubbles of carbonic anhydride being formed, as was pointed out by Davy, which adhere to the crystals, and if the latter are small, carry them to the surface. Dalton found that a saturated solution of the acid carbonate dissolves carbonic anhydride to the same extent that water does; and concluded therefrom that no ammonium carbonate could be formed containing more acid than this carbonate. I think, however, that Dalton's statement as to this solubility of carbonic anhydride must be considered erroneous, a saturated solution of acid carbonate being apparently a saturated solution of carbonic anhydride: indeed, from this fact John Davy doubted that the acid carbonate really existed in solution. A saturated solution of acid carbonate crystallises out when cooled. A solution of the acid carbonate, when heated in a retort, first evolves carbonic anhydride, and then a distillate of normal carbonate (Berthollet), and lastly, one of pure water.

Behaviour with Alcohol.—Acid carbonate is in reality very slightly, if at all, acted on by strong aqueous spirit, cold or boiling. In the cold, the spirit, after digestion, contains a very little caustic ammonia; while a few bubbles of gas, presumably carbonic anhydride, are found entangled among the crystals of the salt. The crystals boiled with the spirit are slowly decomposed, as they would be by the heat alone; carbonic anhydride and ammonia escape, and the remaining spirit is left weakened, and with a little caustic ammonia dissolved in it.

Behaviour with Ammonia.—Dry crystals of the acid carbonate are not acted on by ammonia gas, either at ordinary temperatures, or that of 0° C.

When the powdered salt and strong solution of ammonia are brought together, a hissing sound is produced, the mixture becomes warm, and the salt cakes together and shows little evidence of being dissolved. The salt shaken up to prevent caking, with about six times its weight of solution of ammonia, s. g. ·880, in a closed flask, and then packed in ice for two hours, yielded a sediment about half as bulky again as the original salt; and a supernatant mother-liquor, which had studded the

sides of the flask with brilliant, but very minute, crystals. In a repetition of this experiment the same results were obtained. In a third experiment, to a quantity of the ammonia solution, equal to that employed in the previous experiments, twice as much acid carbonate as was used in them was added, with the result that a greater quantity of sedimentary matter was yielded, but with no very marked increase in the quantity of the crystals which formed on the sides of the vessel. These crystals are not permanent in their mother-liquor, whether kept in ice or not, becoming opaque and devoid of crystalline form in about twelve hours.

As to the nature of the sediment I have no doubt, both from its appearance and the circumstances of its production, and from the already described effect of ammonia-water on the commercial carbonate. The crystals formed on the sides of the vessel can hardly be supposed to be anything else than either the normal carbonate or the carbamate. Those obtained were too small for their forms to be clearly seen; but they were quite different in appearance from the normal carbonate, and very like crystals of the carbamate. The facts, direct and indirect, that may be adduced in support of the view that they are the carbamate are—that the acid carbonate is resolved into carbonic anhydride and normal ammonium carbonate by cold water alone; that carbonic anhydride and ammonia, in the presence of excess of solution of the latter, form carbamate, in spite of the presence of water;* that the solid carbamate can be crystallised out from its solution in ammonia-water; that so far from the tendency of the carbamate to assume water being very great in the presence of free ammonia, the carbonate in solution can itself be readily converted by dehydration into the carbamate, as has been already shown; that it is unlikely from the circumstances of its formation to be anything else but the carbamate, except the normal carbonate, which it is quite unlike; and lastly, that it is just like the carbamate in appearance, so far as the minute size of its crystals has allowed this to be determined. But a material difficulty in believing these crystals to be the carbamate lies in the fact that ice-cold ammonia-water dissolves the solid carbamate in much greater quantity than

* A fact already recognised, but one which I have succeeded in establishing on much more conclusive evidence than has hitherto been obtained, as will be seen farther on in this paper.

can be formed in the case in question, according to the following equation :

$$2CO_2OH_2NH_3 + 2NH_3 = CO_2(OH_2)_2(NH_3)_2 + CO_2(NH_3)_2.$$

By digesting the acid carbonate with the strongest solution of ammonia in a closed vessel, at a temperature of 20°—25°, ammonium carbamate is slowly formed in considerable quantity. The mode of procedure is exactly similar to that already described for converting the normal carbonate into the carbamate; as are also the results, except that, as might be anticipated, the yield of the carbamate is greater. In the first stage of the reaction, by which the carbamate is formed, the acid carbonate and the ammonia probably react, as already represented, to form carbamate and normal carbonate; in the second stage, the normal carbonate thus formed changes into water, and carbamate, as was explained when treating of the reactions of the normal carbonate. Representing the change by a single equation between the substances employed and those finally obtained, we have—

$$CO_2OH_2NH_3 + NH_3 = CO_2(NH_3)_2 + OH_2.$$

A salt in beautiful crystals, to which, although I have not myself succeeded in preparing it, I wish to recall the attention of chemists, was obtained by Rose from an aqueous solution of the commercial carbonate, which yielded a smaller proportion of ammonia than that of one atom to one of carbonic anhydride. Rose found its preparation very uncertain, and only succeeded very rarely in getting it. He obtained it by evaporating the solution of commercial carbonate in a partial vacuum over oil of vitriol, taking care to avoid the production of ebullition in the solution, as this is attended with the formation of the ordinary acid carbonate. He observed that the salt soon changed into the ordinary acid carbonate, when it was left exposed over the oil of vitriol after it was formed; and that it also underwent this change, though more slowly, in whatever way attempts were made to preserve it, the change being marked by efflorescence. In the following table, the percentage results of Rose's analyses are given side by side with the numbers calcu-

lated for two formulæ, (1) and (2), proposed by Rose, and another, (3), which I suggest instead:—

	I.	II.	III.	IV.	Calculated. (1.)	(2.)	(3.)
Carbonic anhydride	—	55·83	—	57·33	55·62	57·06	61·11
Ammonia	19·12	—	18·47	—	19·10	19·60	18·89
Water	—	—	—	—	25·28	23·34	20·00
					100·00	100·00	100·00

(1.) $(CO_2)_9(OH_2)_{10}(NH_3)_8$
(2.) $(CO_2)_9(OH_2)_9(NH_3)_8$
(3.) $(CO_2)_5(OH_2)_4(NH_3)_4$

Though the composition of this salt is an unusual one, I do not think that we can refuse to admit that Rose actually obtained it, seeing that he not only prepared it on different occasions, but made several analyses of it, and observed its efflorescence into the ordinary acid carbonate. On the other hand, I think the facts of its instability, its likelihood of being mixed with crystals of the ordinary acid carbonate, and the material variation in the amounts he obtained of both the ammonia and the carbonic anhydride, render it pretty certain that he analysed not a pure salt, but one mixed with the ordinary acid carbonate. This being admitted, the formulæ proposed by him must be rejected, inasmuch as they severally correspond so closely with the results of his analyses, and in fact differ from them in having rather *less* carbonic anhydride, and *more* ammonia, instead of the contrary. I therefore suggest formula (3) as the most probable one for this salt in the pure state; because, firstly, it implies that the salt as obtained was mixed with a good deal of the ordinary acid carbonate, from the two circumstances mentioned; and secondly, that it represents the salt as being the fourth in the series of carbonates of ammonium which crystallise from water.

In repeating Rose's experiment, I have only obtained crystals which were not the hyper-acid carbonate, but the ordinary one; as they were permanent on exposure, and exactly like the usual crystals of this carbonate. Rose, however, very often failed himself to get anything but the ordinary acid carbonate, as I have already mentioned.

Deville declines to admit the existence of several of Rose's

carbonates as true chemical compounds, on the ground among others, that they were products of distillation. But this objection cannot be brought against the existence (also disputed by him) of this salt, since it was obtained crystallised from solution. It is well to point out here, too, that whereas the products of distillation can readily from their composition be represented as mixtures, such a mode of representation is not possible with this salt.

Constitution of the Carbonates of Ammonium.

Regarded as salts of dibasic carbonic acid, the first and third of the carbonates now described constitute the normal and acid ammonium salts, the former with one atom of water of crystallisation, thus :—

Normal carbonate $CO_3(NH_4)_2,OH_2$
Acid carbonate $CO_3(NH_4)H$

The second carbonate, described under the name of half-acid carbonate, and generally called the sesquicarbonate, is one of a very limited series of salts. Its composition is such that it can only be represented by a formula equivalent to that of a compound of the normal and acid carbonates. Thus :—

$$(CO_2)_3(OH_2)_4(NH_3)_4 = (CO_3)_3(NH_4)_4H_2,OH_2$$
$$= [CO_3(NH_4)H]_2CO_3(NH_4)_2,OH_2.$$

Accordingly, it and the other half-acid carbonates of the alkalies are generally represented as combinations of the normal with the acid salt. Now, as a double salt, the half-acid carbonate has the unusual constitution of one atom of one carbonate united with two atoms of another, both carbonates being salts of monovalent basic radicals. Besides, regarded from this point of view, the half-acid carbonate does not appear to hold a position in the series of carbonates half-way between the other two, but one approaching that of the acid carbonate. When the old atomic weights were in use, the half-acid carbonate was, however, represented as lying equally between the acid and normal salts, in consequence of the atom of acid carbonate being formulated as of double its present proportion to that of the normal carbonate, thus :—

	Old notation.	New notation.
Normal salt ..	$NH_4O,CO_2 + HO$	$CO_3(NH_4)_2,OH_2$
Acid salt	$NH_4O,HO,2CO_2$	$CO_3(NH_4)H.$

In fact, the change made in the values of the atomic weights of the elements has caused the carbonates to be compared by a different standard. Whilst formerly the constant element for determining their constitution was the basic radical, it is now made to be the acid one.

Making the quantity of basic radical a constant, and using the modern atomic weights, the series of ammonium carbonates stands thus:—

Normal carbonate .. $(CO_3)_2(NH_4)_4\ ,(OH_2)_2$ or $(CO_2)_2(OH_2)_4(NH_3)_4$

Half-acid carbonate .. $(CO_3)_3(NH_4)_4H_2,OH_2$ or $(CO_2)_3(OH_2)_4(NH_3)_4$

Acid carbonate $(CO_3)_4(NH_4)_4H_4$ or $(CO_2)_4(OH_2)_4(NH_3)_4$

Here the half-acid salt appears as the true mean of the other two; but then these have formulæ which may appear to be otherwise needlessly complex. However, by representing the half-acid carbonate as a double salt of the other two, this objection is partly removed:

Normal salt	$CO_3\ (NH_4)_2\ ,OH_2$
Acid salt	$(CO_3)_2(NH_4)_2H_2$
Half-acid salt....	$(CO_3)_3(NH_4)_4H_2,OH_2$

The most characteristic reaction of the acid carbonate can only be represented as occurring in the quantity expressed by the above formula, namely, the reaction by which, when warmed with a little water, it passes into carbonic anhydride and the normal carbonate, thus:—

$$(CO_2)_2(OH_2)_2(NH_3)_2 = CO_2 + CO_3(NH_4)_2,OH_2.$$

The probably tetrabasic character of carbonic acid in many of its salts is recognised by many chemists. The greatest objection to admitting this tetrabasic character lies, I think, in its showing apparently a dibasic character in a great number of its best defined salts. It is true that phosphoric acid shows beyond dispute different basic powers; but then, in this case, the difference in basicity is accompanied by other differences in properties, and, above all, is manifested—for the most part at least—quite independently of the nature of the base with which

the acid may be brought into combination, and this is not the case with carbonic acid.

This difficulty would be removed were the apparently dibasic salts represented as tetrabasic, and it appears to me that facts in the history of many of these carbonates give support to the supposition that in them carbonic acid is actually tetrabasic. This is particularly the case with the carbonates of ammonium. That which is the normal carbonate of dibasic carbonic acid, with an atom of water of crystallisation, becomes a half-saturated salt of the tetrabasic acid; and that which is the acid salt of the dibasic acid becomes an anhydro-salt of the tetrabasic acid, in accordance with its chemical behaviour; while lastly, the half-acid carbonate of the dibasic acid, with its one atom of water of crystallisation, so oddly associated with the treble molecule of carbonate, becomes a double salt of the other two tetra- or ortho-carbonates, thus:—

Dibasic.	Tetrabasic.
$CO_3\ (NH_4)_2\ OH_2$	$CO_4\ (NH_4)_2H_2$
$(CO_3)_3\,(NH_4)_4H_2,OH_2$	$CO_2(CO_4)_2(NH_4)_4H_4$
$CO_3\ NH_4\ H$	$CO_2\ CO_4\ (NH_4)_2H_2$

The carbonates of sodium show by their reactions and composition the same relationship, except that the half-acid carbonate contains water of crystallisation:—

Dibasic.	Tetrabasic.
$CO_3\ Na_2\ ,OH_2$	$CO_4\ Na_2H_2$
$(CO_3)_3Na_4H_2,(OH_2)_3$	$CO_2(CO_4)_2Na_4H_4,(OH_2)_2$
$CO_3\ Na\ H$	$CO_2\ CO_4\ Na_2H_2$

As regards the carbonates of the alkaline earths, it is well known that calcium carbonate evolves half its carbonic anhydride at a much lower temperature than the rest. Representing calcium carbonate as an anhydro-orthocarbonate, this change may be thus exhibited by symbols:—

$$CO_2CO_4Ca_2 = CO_2 + CO_4Ca_2.$$

Most chemists must have observed that calcium carbonate, precipitated from moderately strong solutions, is at first in a bulky, gelatinous condition, and that while in this state it is much more soluble in water than when it has passed into the crystalline condition. It has always seemed probable to me that this gelatinous precipitate, like most other similar ones,

is hydrated, and that the changes it undergoes, both in the undissolved condition and in solution, into the other form of carbonate, having many times less volume, was the result of dehydration. Assuming such to be the case, we may represent it as—

$$CO_4CaH_2.$$

Lastly, if there be really a compound formed when chalk dissolves in carbonic-acid-water, as it is usually supposed, this may be represented as—

$$CO_3Ca,CO_3H_2 \text{ or } CO_2CO_4CaH_2.$$

We then have the following symmetrical relations between the carbonates of calcium :—

Burnt chalk.....	CO_4Ca_2	$CO_2CO_4Ca_2$	Chalk.
Hydrated chalk ..	CO_4CaH_2	$CO_2CO_4CaH_2$	Dissolved chalk.

Dolomite,

$$CO_2CO_4CaMg,$$

when heated becomes

$$CO_2 + CO_4CaMg,$$

and the latter substance by the action of carbonic-acid-water yields, apparently,

$$CO_2CO_4Ca_2 + CO_2CO_4MgH_2.$$

The magnesian carbonates can be formulated like the calcium salts, but they contain, both simple and double salts, efflorescent water of crystallisation.

It may be objected that the representation of ordinary salts as anhydro-salts is an undesirable complication. To this the obvious answer is, that with the salts of most acids, whatever class of them we represent as ordinary salts, we have to represent the others as either anhydro-salts, or as basic or oxy-salts. For example, with the salts of the acid in question we must either recognise a number of anhydro-salts, or else a number of basic salts.

If we admit with Rose the existence of a salt containing a greater proportion of carbonic anhydride than the ordinary acid carbonate contains—and we can hardly refuse to do so, as I have already shown—and if, further, we adopt for it the formula $(CO_2)_5(OH_2)_4(NH_3)_4$, proposed by me, instead of either of those suggested by Rose—$(CO_2)_9(OH_2)_{10}(NH_3)_8$ and $(CO_2)_9(OH_2)_9$

$(NH_3)_8$—it will form the fourth member of the series of carbonates of ammonium which crystallise from their solutions:—

$$(CO_2)_2(OH_2)_4(NH_3)_4 \text{ or } [CO_4(NH_4)_2H_2]_2$$
$$(CO_2)_3(OH_2)_4(NH_3)_4 \text{ or } CO_2\ [CO_4(NH_4)_2H_2]_2$$
$$(CO_2)_4(OH_2)_4(NH_3)_4 \text{ or } (CO_2)_2[CO_4(NH_4)_2H_2]_2$$
$$(CO_2)_5(OH_2)_4(NH_3)_4 \text{ or } (CO_2)_3[CO_4(NH_4)_2H_2]_2$$

The regularity of this series, which includes all the carbonates of ammonium yet obtained crystallised from solution, is remarkable, and favours the theory that the half-acid, acid, and hyper-acid carbonates are anhydro-compounds of the normal carbonate. If it be objected that it is improbable that an anhydride and water can exist together in a salt, I reply, firstly, that I do not literally believe this myself, holding that every chemical substance is homogeneous throughout its mass, and not composed of several kinds of matter associated together, and that in using language implying the compound nature of a substance, I do so only to express certain facts in its history, according to the conventional usage of chemists; and, secondly, that, probable or not, the acid and half-acid carbonates do, as matters of fact, resolve themselves into anhydride and normal salt, and that the suggested formula for the acid carbonate indicates this property.

As to the existence of a Normal Ortho-carbonate of Ammonium.—If the normal meta-carbonate can really be considered to be an acid ortho-carbonate, then a normal ortho-carbonate, that is, a salt having the formula—

$$CO_4(NH_4)_4$$

may be supposed to exist. Evidence of its probable existence is not altogether wanting. John Davy pointed out that by treating the commercial carbonate with aqueous spirit, acid carbonate is left undissolved, and a solution of ammonia and carbonic acid obtained equivalent to caustic ammonia and normal meta-carbonate. I have fully satisfied myself of the correctness of this statement. Spirit acts upon the solid normal carbonate in the same way. Also, when added to an aqueous solution of the commercial or the normal carbonate, spirit precipitates the acid carbonate, and leaves a solution more alkaline in composition than that of the normal meta-carbonate. Further, when pearl-ash is distilled with its equivalent, or more, of

sal-ammoniac and aqueous spirit, according to the formula that used to be in the London Pharmacopœia for preparing the *spiritus ammoniæ aromaticus*, the first portions of the distillate —which is a solution of normal meta-carbonate, or one equivalent to it—separate into a more basic solution and crystals of the half-acid and the acid carbonates.

But the action of alcohol is not necessary to cause a solution of normal meta-carbonate (or one equivalent to it in composition) to resolve into an acid carbonate and a more basic solution. When water has been repeatedly treated with fresh quantities of commercial carbonate, as already described, and one or two batches of crystals of half-acid meta-carbonate have been obtained, the mother-liquor is found to be a solution containing a little more than two atoms of ammonia to one of carbonic anhydride. Proof of this will be given presently.

Now, it seems to me much less probable that in these cases the normal meta-carbonate resolves itself into the acid or half-acid carbonate and caustic ammonia, than into one of these salts, and the normal ortho-carbonate (or perhaps the triammonium ortho-carbonate), thus—

$$\overset{\text{Norm. metacarb.}}{4CO_2(OH_2)_2(NH_3)_2} = \overset{\text{Norm. orthocarb.}}{CO_2(OH_2)_2(NH_3)_4} + \overset{\text{Half-acid metacarb.}}{(CO_2)_3(OH_2)_4(NH_3)_4} + 2OH_2.$$

The admission of the formation of a normal ortho-carbonate in this way, does away with the necessity otherwise of holding the half-acid meta-carbonate to be wholly insoluble in a cold concentrated solution of normal meta-carbonate; since we can then equally well regard the mother-liquor of the half-acid meta-carbonate crystals to be a solution potentially of the half-acid meta-carbonate and the normal ortho-carbonate,—and therefore of the same salt as that it has deposited in crystals—as we can regard it to be a solution of the normal meta-carbonate and free ammonia.

Ammonium Carbamate.

History.—Who discovered that ammonia and carbonic anhydride unite to form a solid I do not know. Gay Lussac first determined the proportion in which these gases combine.

Preparation.—(*a.*) By the direct union of dry ammonia and carbonic anhydride gases, when it is deposited partly as an in-

crustation on the walls of the vessel in which it is formed, and partly as flocculi. This is the earliest method known.

(*b.*) (Rose's method.)—By distilling together ammonium sulphamate and anhydrous sodium carbonate, when it is also obtained as an incrustation on the walls of the condensing vessel.*

(*c.*) (Kolbe and Basaroff's method.)—By passing carbonic anhydride and ammonia gases, both perfectly dry, into cold absolute alcohol, separating the copious crystalline precipitate by filtration from the greater part of the liquid, and heating it with absolute alcohol in a hermetically-sealed tube to 100° or above, when the liquid on cooling deposits the carbamate in large crystalline laminæ.† I have not repeated any of these processes. I am able to add to them several others made out by myself.

(*d.*) By passing carbonic anhydride and ammonia gases into concentrated aqueous solution of ammonia, when the carbamate separates in crystals, which when dried as well as possible by pressure between folds of bibulous paper, contain only a little carbonate. The details of the operation are as follows:—A wide-mouthed short-necked flask or bottle, fitted with perforated vulcanised stopper, through which two glass tubes pass, is half-filled with the strong solution of ammonia of commerce, and placed in a vessel of cold water, or, preferably, ice. Carbonic anhydride gas, which has been passed through oil of vitriol, is then sent into the ammonia-water by one of the leading tubes, pushed down nearly to the bottom of the solution. No fear of the ammonia passing up the tube by absorption need be felt, so long as the stream is not exceedingly slow. A stream of ammonia gas—by preference, partly or completely dried—is then sent into the solution by the other leading tube, also dipping deep into the liquid. The flow of the ammonia is regulated to suit the absorption of it that takes place by the liquid. The carbonic anhydride is not absorbed at first much more rapidly than it would be by water, and even after awhile, when its rate of absorption has considerably increased, it can still be sent through the liquid to the surface with ease; this it is ad-

* Poggendorff's Annalen, vol. xlvi, p. 373. Also Taylor's Scientific Memoirs, vol. ii, p. 98.

† Direct conversion of Ammonia Carbamate into Urea. Journal of the Chemical Society (2), vol. vi, p. 194.

vantageous to do, as its absorption is completed at the surface of the solution, unless it is sent into it in very large quantity. When the solution is kept cool by ice very little incrustation forms on the sides of the bottle above the liquid, but when the solution is not kept cool, a thick incrustation is formed. The carbamate soon precipitates in small crystals in the cold solution, but in the warm solution this does not take place for some time. This, however, is only because the carbamate is more soluble in the warm liquid; for it crystallises out on the cooling of the solution. But, as the carbamate more easily combines with water when in solution, it is desirable to keep the solution cool, so that it may be precipitated as soon as possible after it is formed. When the solution containing precipitated carbamate is allowed to grow warm, the greater part or all of the carbamate re-dissolves, but separates again on cooling. A little normal carbonate usually separates along with the carbamate. This can be partly separated from the heavier crystals of the latter by decanting the solution, after agitation, from the carbamate before much of the carbonate has had time to settle down. The incrustation on the sides of the bottle is also carbamate, but more contaminated with carbonate. The crystals of carbamate are strained off and pressed in a calico filter, and then dried by pressure between folds of bibulous paper. They cannot be obtained quite dry. They are to be stored in a closely-stoppered bottle, and during the first few days they must be shaken about, or otherwise they will cake together, by slowly uniting with the adhering moisture to form carbonate. The stopper must also be turned occasionally, as it is very apt to get cemented into the bottle by a little carbonate forming between it and the neck. The yield of carbamate by this process is good, but the carbamate is never very pure, having some carbonate formed along with it during its preparation, and more afterwards from the moisture which always adheres to it. It is worthy of notice that in this process we have an exact imitation of the process (*c*) employed by Kolbe and Basaroff, only that concentrated ammonia-water is employed instead of absolute alcohol.

(*e*.) By digesting in a closed vessel an aqueous solution of ammonia, saturated with the gas at a low temperature, with either the commercial carbonate, or any other carbonate of ammonium, at a temperature of 20°—25° for thirty-six or forty

hours, when the carbamate either crystallises out at once on cooling, or will do so after cooling the solution, passing more ammonia gas into it, adding more carbonate, repeating the digestion as before, and then again cooling. This process has been already described in the account of the reactions of the normal and acid carbonates. The best carbonate to employ is the commercial carbonate, because it yields more of the carbamate, as might be anticipated from its composition. The crystals are the same as those obtained by process (*d*), but usually much larger. Large crystals can be obtained almost perfectly dry, and quite free from admixture with the normal carbonate (which is always formed with the carbamate by this method, though in very small quantities).

(*f*.) By heating the commercial carbonate of ammonia mixed with a sufficient quantity of anhydrous potassium carbonate in a retort, immersed in a water-bath at a temperature carried slowly from about 50° to about 80°, and connecting the neck of the retort with a wide tube dipping under mercury, when the neck of the retort becomes incrusted with the carbamate in a translucent crystalline condition. The water-bath is to be maintained at a temperature not much exceeding 60° C. until ammonia gas, which is at first generated in large quantities, has nearly ceased to escape through the mercury. The temperature of the bath is then to be raised, but not so rapidly as to cause any material escape of gas through the mercury. The potassium carbonate is to be freshly ignited, and in powder, and to be mixed with less than its bulk of the commercial carbonate, in good condition and crushed small, and the mixture covered with a layer of the potassium carbonate. To obtain the carbamate, the neck of the retort is to be cut off and broken up, and the carbamate chipped from the fragments. If the neck of the retort is kept cool by special means, the carbamate is formed more rapidly than if these means are not employed; but it is then not so crystalline, and adheres with such increased firmness to the glass, that much time is spent in detaching it, during which it is absorbing moisture. I have not obtained the carbamate quite pure by this process, but it has been markedly purer than the carbamate obtained by Rose from the mixed dried gases.

(*g*.) By distilling, as in the last process, a mixture of the commercial carbonate of ammonia and anhydrous calcium chloride,

when an incrustation forms, similar in every respect to that obtained in the last case, which is the carbamate. At a temperature of the water-bath of about 48° a considerable quantity of carbonic anhydride escapes through the mercury, and at about 52° the incrustation begins to form, and continues to do so with very little further escape of gas, while the temperature is allowed to rise very slowly to 65°, a temperature which is sufficient to carry the process to its completion. The calcium chloride used is to be in as fine a powder, and as nearly anhydrous as possible; and it must be used in considerable excess, as particles of it are only acted on superficially. The mixture with the carbonate can be effected by shaking the two powders in a stoppered bottle, so as to avoid unnecessary exposure to the air.

I have used of the calcium chloride from one-and-a-half to three times the weight of the carbonate, and generally reserved some of it to cover over the mixture of the carbonate with the rest. The carbamate is generally very nearly pure, provided sufficient anhydrous calcium chloride has been used. When not very pure, it can be rendered almost perfectly so by distilling it off fresh calcium chloride. The yield of carbamate is less than that by the previous process.

(*h.*) By distilling the commercial carbonate extremely slowly, when the more remote part of the earlier formed incrustation will be found to be impure carbamate. I have obtained samples from an incrustation thus prepared, in which six-sevenths and five-sixths respectively of the contained ammonia were in the state of carbamate. There are no sensible qualities by which the composition of the product can be inferred, so that it is quite possible, indeed more probable than not, that parts of the incrustation were more nearly pure carbamate than the samples selected for analysis proved to be. This process is, of course, only of interest from a theoretical point of view. The product obtained by Rose by a similar process is not the same as that obtained by me, a fact which admits of a ready explanation, as will be presently seen. (Pp. 234, 239.)

(*i.*) By distilling the normal carbonate at a heat not exceeding 60°, when a solid condenses containing even less water than the product of method (*h*). I shall have again to refer to this product of the distillation of the normal carbonate, and shall endeavour to show that the pure carbamate is really formed at first, its hydration being a secondary matter.

(*i.*) By repeatedly dissolving commercial carbonate at a gentle heat in the same quantity of water, cooling after each addition, and separating the crystals, as already described, until crystals of normal ammonium carbonate are deposited; then once more warming the solution, dissolving a fresh quantity of commercial salt in it, allowing it to cool and crystallise for a day, separating the crystals, passing ammonia gas, straining off or not (as may be necessary) the precipitate of normal carbonate produced, renewing or continuing the stream of ammonia till the solution (kept cool) is about saturated, and straining off the precipitate of normal carbonate, when the solution will prove by its reactions to be apparently a solution of carbamate with a little carbonate dissolved in it. I think it not unlikely that by carrying this process further, with some modification, crystals of carbamate might be obtained; but I have made no experiments in this direction.

(*k.*) By distilling the commercial carbonate with strong spirit, or, probably better still, with absolute alcohol. The details of the process will be given when treating of the commercial carbonate and the products of its distillation. The carbamate is wet—mixed with water and spirit—but contains very little carbonate.

Sensible Qualities.—Ammonium carbamate has a strong smell of ammonia, but not at all equal to that of the normal, or even half-acid, carbonate. As regards its taste also, it is strongly ammoniacal, but without the causticity of the normal carbonate.

Form.—It occurs in the form of flocculi; of an incrustation more or less crystalline; of prisms found sometimes projecting from this incrustation; of crystalline laminæ (Kolbe and Basaroff); and of crystals neither tabular nor decidedly elongated or columnar.

Of the system of the last-named crystals, I am unable to speak with any degree of assurance, but they seem to belong to either the right or the oblique rhombic prismatic system. They frequently occur massed together, like crystals of alum, one crystal capping the other, as it were. When solitary they are not only of no great size, but also are rapidly deprived of their angles and edges by the changes they undergo. When their growth is not interfered with by contact with each other and with crystalline particles of the normal carbonate,

they are perfectly transparent. The incrustation consists of prisms arranged perpendicularly to the surface of formation. The translucency of the mass attains a high degree of perfection in those parts formed nearest to the source of heat. Fragments from this part of the incrustation appear almost perfectly transparent when thrown into water. In appearance this form of the carbamate differs little, if at all, from a similarly formed deposit of acid-carbonate—with one exception. This is in the parts formed near the source of heat, which acquire an increased translucency by the continued action of the heat employed in carrying on the process, and also undergo marked contraction, so as to exhibit gaping fissures, and become partly separated from the walls of the retort on which they rest. This phenomenon is always observed in the carbamate, whether formed by the action of potassium carbonate or calcium chloride, and never with hydrated incrustations, according to my experience. The prisms which sometimes project from the free surface of the incrustation are thick and generally very short, but sometimes they pass right across to the opposite wall of the retort-neck or condensing-tube.

Chemical Composition.—It is unnecessary for me to adduce evidence to prove that ammonium carbamate is composed, according to the formula—

$$CO_2(NH_3)_2,$$

of

Carbonic anhydride.....	56·41
Ammonia	43·59
	100·00

All that I shall give under this heading are the details of my analyses of samples of carbamate obtained in different ways, in order to show their degree of purity. For brevity, the letters (*d*), (*e*), (*f*), &c., are employed to indicate by what method, thus distinguished, the sample was prepared.

(*d.*) 1·3252 grms. treated with hydrochloric acid, gave to soda-lime ·7115 grm. of carbonic anhydride, and on evaporation 1·7260 grms. of ammonium chloride, = ·5489 grm. of ammonia.

·9930 grm. of the product of another experiment neutralized a volume of standard solution of sulphuric acid, equivalent to ·4097 grm. of ammonia.

1·0728 grms. of a third preparation neutralized a volume of standard sulphuric acid, equivalent to ·4420 grm. of ammonia.

(Several samples of the incrustation on the sides of the bottle and of the crystalline deposit formed when the ammonia-water was not kept cool, visibly mixed with a little carbonate, were analysed with results showing a greater degree of impurity.)

(*e.*) ·3037 grm. of crystals obtained from the commercial carbonate neutralized a volume of standard acid, equivalent to ·1318 grm. of ammonia.

·7365 grm. of crystalline masses, which I could not thoroughly dry on account of the large surface exposed when they were crushed down, gave ·4039 grm. of carbonic anhydride.

·3568 grm. of the same preparation neutralized a volume of acid equivalent to ·1527 grm. of ammonia.

(*f.*) ·5521 grm. treated with hydrochloric acid, gave ·7384 grm. of ammonium chloride, = ·2348 grm. of ammonia.

·9693 grm. of a different part of the same incrustation gave ·5354 grm. of carbonic anhydride and 1·2967 grms. of ammonium chloride, = ·4124 grm. of ammonia.

·9470 grm. of a different part of the same product gave ·5257 grm. of carbonic anhydride, and 1·2773 grms. of ammonium chloride, = ·4062 grm. of ammonia.

(*g.*) ·8567 grm. neutralized a volume of standard sulphuric acid, equivalent to ·3536 grm. of ammonia.

·7450 grm. of another part of the same preparation neutralized a volume of standard sulphuric acid, equivalent to ·3062 grm. of ammonia.

1·0779 grms. of another preparation (for which a much greater proportion of calcium chloride had been used), neutralized a volume of standard sulphuric acid, equivalent to ·4651 grm. of ammonia.

·8046 grm. of another part of the same preparation neutralized a volume of standard sulphuric acid, equivalent to ·3485 grm. of ammonia.

·6130 grm. of another preparation neutralized a volume of standard sulphuric acid, equivalent to ·2610 grm. of ammonia.

·7070 grm. of another preparation neutralized a volume of standard sulphuric acid, equivalent to ·3035 grm. of ammonia.

(*h*.) 1·0495 grms. of a sample of the outer layer of the remote part of the incrustation yielded, with hydrochloric acid, ·5758 grm. of carbonic anhydride, and 1·2300 grms. of ammonium chloride, = ·3912 grm. of ammonia.

·9327 grm. of another sample, similarly selected from the same incrustation, yielded, with hydrochloric acid, ·5085 grm. of carbonic anhydride, and 1·0612 grms. of ammonium chloride, = ·3375 grm. of ammonia.

(*i*.) 1·0073 grms. gave ·5515 grm. of carbonic anhydride, and 1·2730 grms. of ammonium chloride, = ·4049 grm. of ammonia.

(*k*.) Of this product of distillation, from which much of the spirit had been removed by setting fire to it, but which was still wet and unchanged in appearance (see account of this distillation near the end of the paper), 1·2845 grms. of the inner part neutralized a volume of standard sulphuric acid equivalent to ·4939 grm. of ammonia.

Rose made analyses of the carbamate prepared by methods (*a*) and (*b*). The results of his analysis of the product of (*a*) are given in the following table. Of the product of (*b*) he merely states that it proves to be as pure as that obtained by method (*a*). Of the product of method (*c*) Basaroff is stated to have found the composition to be exactly that indicated by the formula for the ammonium carbamate.

		Carb. anhyd.	Ammon.
Rose	*a* I	55·45	—
	a II	—	41·69
	a III	—	44·79*
	a IV	55·75	—
	d I	53·69	41·42
	d II	—	41·26
	d III	—	41·20
	e I	—	43·39
	e II	54·85	—
	e III	—	42·79
	f I	—	42·53
	f II	55·24	42·55
	f III	55·51	42·89
	g I	—	41·27

* Evidently an error; but it is not a misprint, as it agrees with the experimental quantities.

	Carb. anhyd.	Ammon.
g II	—	41·11
g III	—	43·15
g IV	—	43·31
g V	—	42·58
g VI	—	42·93
h I	54·87	37·27
h II	54·52	36·19
i	54·75	40·20
k	—	38·45
Calc.....	56·41	43·59

Behaviour on Exposure.—It evolves an odour of ammonia which, when a solid lump of it, or a crystal, is exposed freely to the air, rapidly diminishes in intensity; at the same time the carbamate gradually deliquesces; by continuing the exposure it is nearly dissipated. The residue left is acid carbonate, generally in the form of a porous cast or superficial skeleton of the original fragment. This is best seen with the carbamate obtained by distillation; while the deliquescence is best seen in the crystals deposited from solution, but not to an extent suggestive of any difference in the two forms of carbamate. According to some writers the carbamate is entirely dissipated by exposure; according to others it leaves, as I have myself observed, a little acid carbonate. In one experiment I exposed ·8726 grm. of carbamate (a sample of which had been found to yield on analysis 43·2 per cent. of ammonia in place of 43·59, the calculated number for the pure salt) for 48 hours, and obtained ·0162 grm. of acid carbonate, of the size and the shape of the piece of carbamate used, but hollow internally. This corresponds to 1·82 per cent., and included whatever acid carbonate was in the fragment when first exposed, plus a little moisture, and minus some acid carbonate that must itself have been dissipated during the exposure.

The deliquescence of the carbamate is an interesting fact, not only as affording further evidence that the carbamate has only a slowly-manifested chemical affinity for water, but also as distinguishing between the mere physical attraction of a body for water, and its chemical transformation with water into a new substance.

To observe the deliquescence of the carbamate, the exposed

fragments or crystals should be pressed after about an hour's exposure, when a superficial film of acid carbonate, which gives the appearance of dryness and solidity to it, is broken through, and a drop of fluid forced out. That this deliquescence is not accompanied by any material chemical hydration of the carbamate is shown by the fact that so little acid carbonate is left on further exposure, which would not be the case if ammonium carbonate solution were left to dry up. It is to its dissipation by exposure, and its deliquescence, that the difficulty of determining the form of its crystals is due. So far as the conversion into acid carbonate takes place, it may be thus represented :—

$$CO_2(NH_3)_2 + OH_2 = CO_3(NH_4)H + NH_3,$$

or

$$CO(NH_2)(ONH_4) + (OH)H = CO(OH)(ONH_4) + (NH_2)H.$$

Behaviour when Heated.—Ammonium carbamate, unlike the true carbonates, does not fuse when heated. According to John Davy it is converted into gas at 60° C. My own experiments very nearly confirm this statement. I was not able to fix the point very closely, but found it to be about 59°. The method I adopted to determine this point was to pass a fragment of carbamate up into a tube full of and inverted over mercury, surrounding the tube with water, and then heating this, as in Gay Lussac's method for taking the specific gravity of vapour. The height of the mercury in the tube did not seem to have any material effect upon the point of volatilization.

When carbamate is converted at any temperature into gas or vapour it appears to be decomposed into carbonic anhydride and ammonia. I consider we should have been justified in believing that it is decomposed when dissipated at ordinary temperatures, because of the powerful odour of ammonia which is then perceived ; for it is inconsistent with what we know for certain of the change in properties produced by chemical combination, to suppose that a compound of ammonia should smell like ammonia itself. But we have had evidence on this point of another kind for a long time before us, the force of which only few chemists would at present deny. Before describing this it will be convenient to notice part of the evidence as to the nature of the product of the distillation of the carbamate at or above 60°. It has been for many years familiar to chemists

that the volume of this product equals the sum of the volumes of the ammonia and carbonic anhydride gases, which unite to form carbamate; in other words, that the carbamate obtained from two volumes of ammonia and one volume of carbonic anhydride yields three volumes of vapour. A fact like this is now held by most chemists to be proof that a substance thus behaving is decomposed at the moment when it assumes the gaseous state; and indeed ammonium carbamate was one of the principal instances cited by Deville in support of his theory of dissociation, and has since been one of the instances of decomposition in vapours he has selected to illustrate the distinction between "decomposition" and "dissociation" in the more limited sense in which he now uses the latter term. The evidence that I have referred to as having been so long before chemists, and which I think has hardly been recognised by them, that the vapour rising from the carbamate at ordinary temperatures is a mixture of carbonic anhydride and ammonia, and not the vapour of the carbamate itself, is that afforded us in 1838 by Bineau, to whom we are also indebted for the first evidence on the difference in the density of sulphur vapour at high and low temperatures. Bineau took the density of the vapour of the carbamate at ordinary temperatures*—by leaving it in contact with a measured quantity of air at a temperature of 20° or 30° until it had volatilised, and then obtaining the volume of the vapour by treating the mixture first with a solution of oxalic acid, and then with one of potash—and found it accord with the sum of the volumes of the ammonia and carbonic anhydride which form it.

Bineau has also furnished us with special evidence that the vapour, obtained by distilling carbamate, is nothing but a mixture of the two above-named gases. He observed† that the gaseous product obtained by exposing the salt to heat retains its gaseous state at a temperature which is lower than that at which it is formed. I am myself able to confirm this statement and give additional evidence on the subject. In the experiment, just now described, by which I endeavoured to determine the point at which the carbamate becomes a permanent gas, I observed that on allowing the apparatus to cool, the gas

* Recherches sur les densities de Vapeur. Ann. de Chimie, vol. lxviii, p. 416.

† Sur quelques combinaisons ammoniacales et sur le rôle que joue l'Ammoniaque dans les réactions chimiques. Ann. de Chimie, vol. lxvii, p. 240.

produced only slowly condensed as the temperature fell. The condensation was complete before the temperature had fallen below about 55°, but the cooling proceeded only slowly, and I have no doubt that by rapid cooling the gas could have been brought to a much lower point before it condensed. A material imperfection in the evidence afforded by this experiment, which indeed was not made with the object of determining this point, is probably the fact that as the gases condensed, the residue became rarefied by the rising of the mercury to a height of ten or twelve centimètres.

The evidence afforded by another experiment was very striking. When, in distilling some carbamate (containing a little combined water and small excess of carbonic anhydride) off some anhydrous calcium chloride, the temperature of the water-bath, in which the retort was placed, was at about 52° C., and the carbamate was steadily depositing in the neck of the retort at a distance of 7 or 8 centimètres from the source of heat, the heat of the bath was allowed to rise in a quarter of an hour to a point somewhere between 65° and 70°, and then allowed to sink again at about the same rate to 55°. The result was that as the temperature rose, the seat of the condensation of the gases moved down the retort-neck and the tube forming a continuation of it, until it was from 50 to 55 centimètres from the source of heat, and then as the temperature fell moved back again, until it was up to about 12 or 15 centimètres only from the source of heat when the temperature had fallen to about 55°. The position of the seat of condensation was ascertained by the heat given out there, which was roughly estimated to be about 45° or 50°. Between the seat of condensation and the body of the retort, the tube and the retort-neck, except in the parts of the latter near the source of heat, were almost cold, having a temperature estimated as certainly not exceeding about 25°. I think no other conclusion can be come to, but that in this experiment the mixed gases, and not the vapour of the carbamate, were generated in the retort, and that they combined again, with evolution of chemical heat, when they had proceeded some distance along the tube. But a full explanation of the entire phenomenon has not presented itself to me. For I am at a loss to understand how it is that the gases, after escaping condensation in the relatively cool part of the tube, condensed at a point which, though cool at first, soon heated up

to such an extent as it did by the condensation going on there. During the rise in temperature, uncondensed gases escaped in bubbles through the mercury, into which a small exit-tube attached to the extremity of the condensing tube dipped, and during the fall in temperature the mercury rose in the tube. The apparatus was air-tight, and there were only two joints, both made with vulcanised rubber. One of these joints was made with a small perforated stopper, fixing the exit-tube very tightly into the end of the condensing tube; the other was made with a piece of large fleshy tubing surrounding the other end of the condensing tube and the mouth of the retort, which were put as closely in apposition as possible, and this joint was bound with wire. This joint was soon further secured by a firm deposit of the carbamate itself; so that appreciable diffusion could not have taken place. The exit-tube dipping in the mercury had its end turned up, so as to check the escape of any gas between the vertical part of it and the mercury. There must have been present during the operation a very slight excess of carbonic anhydride and a trace of moisture. The sublimate was ascertained to be nearly pure carbamate, and the calcium chloride in the retort to have retained only a minute quantity of ammonia or ammoniacal salt. But whatever be the entire nature of this phenomenon, it is clear from it that the vapour rising from the carbamate is a mixture of carbonic anhydride and ammonia. Unfortunately I have not recently had the opportunity of making a further investigation of this phenomenon.

Behaviour with Water.—One part of ammonium carbamate dissolves in about one-and-a-half parts of water, sensible cold being produced by the solution. It dissolves unchanged, as is shown by the reactions of the solution immediately after it is prepared. But the carbamate in solution soon combines with water and becomes carbonate, according to this equation—

$$CO_2(NH_3)_2 + 2OH_2 = CO_4(NH_4)_2H_2.$$

Behaviour with Alcohol.—Ammonium carbamate is soluble in spirit of sp. gr. ·829, according to John Davy. In absolute alcohol, when heated with it in a sealed tube, it dissolves, and crystallises out when the solution is allowed to cool (Kolbe and Basaroff). I have made no experiments on this subject myself.

Behaviour with Ammonia-water.—It dissolves freely in the strong ammonia-water of commerce, with production of cold. At 15° one part dissolves in a little more than two parts of the ammonia-water. The solution, left to itself for some time, yields crystals of the normal carbonate. But when cooled down to about 0° soon after it is made, it yields the carbamate again in relatively large crystals. Ammonia, therefore, has the power, well marked, of impeding the hydration of the carbamate. To this fact is probably due the success in obtaining the carbamate from the carbonate by heating its solution in presence of ammonia.

Reactions which serve to distinguish the Carbamate from the Carbonates generally.—Rose has pointed out the following:—The carbamate is not perceptibly affected by dry hydrochloric acid in the cold, and warmed in the acid is decomposed without liberation of water. In dry chlorine gas it is not at first affected, but is slowly decomposed without formation of water. It assumes in the cold a pale yellowish colour when placed in sulphurous anhydride. Heated in sulphuretted hydrogen gas no water is produced. It yields carbonic anhydride *without effervescence*, when the vapours of sulphuric anhydride are passed over it.

Besides these, it has a special reaction in solution with calcium chloride; when mixed with anhydrous calcium chloride it can be expelled by a gentle heat, leaving the chloride unchanged; it does not melt or become moist when heated; and it dissolves freely in strong ammonia-water. Its becoming moist on exposure is not characteristic, as both the half-acid and the normal carbonates become moist also, though from a different cause.

Reactions on which the preparation of Ammonium Carbamate depends.—These reactions are essentially either the union of carbonic anhydride and ammonia, or the dehydration of ammonium carbonate. Whatever may be the exact nature of the reaction on which Rose's method depends, the formation of the carbamate by this method makes no exception to this statement, since it cannot be admitted that carbamate exists in the state of vapour.

The reaction between the ammonium sulphamate and the sodium carbonate may be thus compared with that between the sulphamate and a caustic alkali:

$$SO_3(NH_3)_2 + CO_2(ONa_2) = SO_3(ONa_2) + 2NH_3 + CO_2;$$
$$SO_3(NH_3)_2 + ONa_2 = SO_3(ONa_2) + 2NH_3,$$

or

$$SO_3(NH_3)_2 + ONaH = SO_3(ONaH) + 2NH_3$$

The preparation of the carbamate by method (*d*), that is, by the union of the ammonia and carbonic anhydride in the presence of water, is of special interest. That carbamate is thus formed has been pointed out by Kolbe* as probably being the case from the fact that carbonic anhydride passed into a solution of ammonia, does not at first precipitate calcium chloride. His explanation of this fact has not remained unchallenged; and Storer has shown the insufficiency of the evidence on which this opinion has been based.†

The crystallisation, however, of the carbamate out of the solution has now put the fact of its formation beyond dispute.

Debus‡ has found that, in the analogous experiment of passing ammonia gas into an alcoholic solution of sulphide of carbon, the formation of sulpho-carbamate is favoured by a temperature not exceeding 15°, and an excess of sulphide of carbon; and the formation of sulpho-cyanate and sulpho-carbonate by a temperature of 30° to 40,° and an excess of ammonia.

The formation of the carbamate in this way is interesting also, from the light it throws on the nature of aqueous ammonia; for, whatever may be the constitution of the crystals of hydrated ammonia obtained at low temperatures, unless it be maintained that carbonic anhydride resolves an ammonium hydrate into ammonia and water thus—

$$CO_2 + 2OH(NH_4) = CO_2(NH_3)_2 + 2OH_2,$$

instead of combining with it to form ammonium carbonate, ammonia-water cannot be considered to be a solution of ammonium hydrate.

Methods (*e*) are examples of the formation of the carbamate by the dehydration of the carbonate, and probably of the union also of ammonia with carbonic anhydride in the case of the half-

* Handwörterbuch der Chemie, i, supplement, p. 157.

† Dictionary of Chemical Solubilities, p. 110. The discussion of this point, however, would require an account to be given of the behaviour of carbonates and carbamate with calcium chloride, and this I think it better to give in a separate paper, which I will lay before the Society on the first opportunity it will afford me.

‡ Annalen der Chemie und Pharmacie, vol. lxxiii, p. 76.

acid and acid carbonate. The reactions in these cases have already been expressed in symbols. The reaction when the commercial carbonate is employed will be given further on. So also will explanations of the reactions on which methods (*f*), (*g*) and (*i*) depend. The reason for doing so will then be evident. With regard to method (*h*), in which an impure carbamate is obtained by condensing the products of distillation of the commercial carbonate, it must be held to depend on the direct union of carbonic anhydride and ammonia gas, since the carbamate cannot exist in the state of vapour. I shall presently give a full account of the products of this distillation. As neither carbonate nor carbamate exists in the state of vapour, method (*i*) does not depend upon a simple dehydration of the carbonate.

Chemical Constitution of the Carbamate.—Analogy has caused this salt to be regarded by Gerhardt, and most chemists after him, to be like the salts formed by the union of other anhydrides with ammonia; conclusive evidence on this point is still wanting. There are no metallic carbamates known. With calcium chloride, and with barium chloride, it does not, however, behave like ammonium carbonate; and this is probably due to the formation of a not very insoluble calcium carbamate. In connection with this point I may state that by adding to the solution obtained from the commercial carbonate by water—method (*i*)—a concentrated solution of calcium chloride, I have obtained a crystalline precipitate not only somewhat soluble in its mother-liquor, but which after being filtered off and pressed between bibulous paper has sometimes proved almost perfectly soluble in water, though in a few minutes its solution deposited calcium carbonate; it did not smell of ammonia. I am not sure that this precipitate, however, was really calcium carbamate. I made analyses of it in its impure and damp state, not venturing to wash it. The mother-liquor was strongly charged with calcium chloride. The results I obtained indicate the following composition in 100 parts, and atomic proportions :—

Calcium	17·97	or	2 atoms
Chlorine	8·55	„	1 atom
Carb. anhyd.	29·26	„	3 atoms
Ammonia.....	12·00	„	3 „
Water (by diff.)	32·22	„	8 „
	100·00		

The presence of water leaves it uncertain whether the substance is a double carbonate of ammonium and calcium, or the carbamate of calcium. The numbers agree remarkably well with a compound having either of the following formulæ—

$$CO_3(NH_4)_2,CO_3Ca$$
$$(CO_2NH_2)_2Ca$$

mixed with hydrated calcium chloride. A similar precipitate is obtained with barium chloride. The probability, I think, is, that the precipitates are carbamates; and if so the constitution of the ammonium carbamate is that expressed by its name, and by the formula—

$$CO_2(NH_2)(NH_4)$$

Ammonium carbamate may be represented as an ortho-carbamic acid, thus—

$$CO_2(NH_2)_2H_2, \text{ or } C(NH_2)_2(OH)_2.$$

But there is no evidence as yet to support this view of its constitution, unless it be that afforded by the fact that ammonia prevents the passage of the carbamate into carbonate; which may be supposed to be due to the union of the ammonia with this acid to form an ortho-carbamate slightly more stable, according to this equation—

$$C(NH_2)_2(OH)_2 + 2NH_3 = C(NH_2)_2(ONH_4)_2.$$

For the purposes of this paper I have generally found it most convenient to represent the carbamate and the carbonates as combinations of carbonic anhydride and ammonia, and of carbonic anhydride, ammonia, and water respectively. Such a representation is as justifiable as any other.

Let me here also add in explanation that I use the word "constitution," as I do that of "composition," conventionally only. As I do not recognise in any single substance any heterogeneous parts, much less can I recognise any arrangement of them.

"*Carbonate of Ammonia*" *of Commerce.*

It will be more convenient to reserve the consideration of the manufacture of the commercial carbonate until I come to treat of the products of the distillation of substances, or mixtures of

substances yielding compounds of ammonia, carbonic anhydride, and water.

Form.—All I wish to point out under this heading is that the variations in the appearance of this substance, whether between one sample and another, or between different layers of the same sample, are not proofs of any material difference in composition. It may be very compact with a more or less conchoïdal fracture, or in softer cakes of prisms arranged uniformly perpendicular to the surface of deposition, or in white nearly opaque layers, and yet differ no more in composition than two samples of similar appearance. On the other hand, similarity in appearance is no proof of identity in composition ; some of the evidence I have on this point is given in the succeeding paragraphs.

Chemical Composition.—No one has attributed to the commercial carbonate anything like an unvarying composition, but it seems to be universally accepted that this does usually approximate pretty closely to that expressed by the formula—

$$(CO_2)_3(OH_2)_2(NH_3)_4,$$

which has in 100 parts—

Carbonic anhydride	55·93
Ammonia	28·81
Water	15·26

And it cannot be denied that in the main the published analyses of it indicate that such is its approximate composition.

The following table contains most, if not all, of the published results of analyses that I have come across :—

	Date.	Carb. anhy.	Amm.
Bergman*	1774	45·	43·
Dalton*	1813	59·	24·5
Ure†	1817	54·5	30·5
Phillips‡	1819	54·2	29·3
Thomson§	1820	55·70	26·17
John Davy*	1834	54·58	27·39
Rose*	1840	—	28·66
„	—	—	30·70

* Memoir already quoted.

† Annals of Philosophy, vol. x, p. 203.

‡ Quarterly Journal of Literature, Science, and Art, vol. vii, p. 294.

§ A System of Chemistry, vol. ii, p. 413, sixth edition.

	Date.	Carb. anhy.	Amm.
Rose	—	50·55	—
„	—	53·40	—
„	—	56·23	—
Ure*.....	1853	55·89	28·86

Dalton deduced from his numbers the atomic composition since universally adopted; and if these numbers are compared with those he used to express the composition of the acid carbonate, they are found to agree closely enough with the calculated numbers.

Dr. Thomson† erred in stating that Dalton considered the commercial carbonate to be a "subtricarbonate," that is, a compound of one atom of carbonic anhydride with three of ammonia, according to the present, as well as Dalton's system of atomic weights. He indeed stated that he obtained a solution of such a subtricarbonate, but this had nothing whatever to do with the commercial salt, to which he not only gave the atomic constitution since adopted, but moreover described it as equivalent in composition to one atom of "subcarbonate" (acid carbonate) and two of "carbonate" (carbamate), just as others have regarded it since.

Dalton read his paper on this subject in 1813, but it was not published till 1819. In the mean time Ure published the results of his analysis of the commercial carbonate, and was followed by Phillips, who published results obtained by himself, confirming those of Ure. Phillips had before this given the results of an analysis of the carbonate, but these, after Ure had published his results, he considered to be erroneous. Ure gave afterwards in his Dictionary the results of analyses made by him which differ from those which he first published. The results of the earlier analyses of Ure, those of Phillips's analyses, and some of those of Rose's analyses, indicate a compound containing a greater proportion of ammonia than that of four atoms to three of carbonic anhydride. Besides this, the majority of the results show the presence of a little water in excess of that indicated by the adopted formula.

I have analysed several samples of the carbonate at present

* A Dictionary of Arts, Manufactures, and Mines, fourth edition. Art. "Carbonate of Ammonia."

† Annals of Philosophy, vol. xv, p. 137.

in commerce, and have found that it is very uniform in composition, with one special exception, and that this composition is no longer that represented by the formula,

$$(CO_2)_3(OH_2)_2(NH_3)_4,$$

but that expressed by the simpler formula,

$$(CO_2)_2OH_2(NH_3)_3.$$

This formula, represented by the symbols of the old atomic weights, becomes more complex than the other formula similarly represented; thus,

1st formula, old notation $(CO_2)_3(OH)_2(NH_3)_2$
2nd formula, old notation $(CO_2)_4(OH)_2(NH_3)_3$

This, I think, had some influence on the selection of the formula. For Ure's analysis, which both here and abroad seems to have been the first which enabled chemists to adopt a formula for the commercial carbonate, agrees much more closely with the second formula than with the first. But then the first could be represented by the formula of an ammonium salt, thus,—

$$2NH_4O,3CO_2$$

—while the second could not. However, the results of other analyses corresponded more nearly with the formula adopted, and so strengthened the grounds of its selection.

The samples I have analysed were purchased at intervals over a period of two years or more, of different firms (though not of the manufacturers direct), at different prices and of different qualities. Small fragments, quite free from decomposed portions, were broken from the inside of lumps just before they were used for analysis. The following are the details and results of my analyses:—

The contents of one of the 7 lb. jars usually made up for the use of dispensing chemists, found to consist of fragments of a cake exhibiting different layers: (*a*), the outer layer, constituting the greater thickness of the cake, compact, translucent, imperfectly crystalline, and of conchoïdal fracture; (*b*), a much thinner layer, friable, semi-opaque; (*c*), a layer, apparently the innermost of the cake, hardly 2 millimètres thick, very translucent, prismatically crystalline:—

I. 1·085 grms. of (*a*) yielded, with hydrochloric acid, ·5952 grm. of carbonic anhydride to soda-lime;

II. 1·1600 grms. of (*a*) neutralized a volume of standard sulphuric acid, equivalent to ·3783 grm. of ammonia;

III. 1·0904 grms. of (*a*) neutralized a volume of standard sulphuric acid, equivalent to ·3570 grm. of ammonia;

IV. 1·1437 grms. of (*a*) yielded with hydrochloric acid 1·1680 grms. of ammonium chloride, = ·3715 grm. of ammonia;

V. ·9063 grm. of (*b*) yielded, with hydrochloric acid, ·5006 grm. of carbonic anhydride to soda-lime;

VI. 1·0538 grms. of (*b*) neutralized a volume of standard sulphuric acid, equivalent to ·3468 grm. of ammonia;

VII. 1·4405 grms. of (*b*) gave, with hydrochloric acid, 1·4957 grms. of ammonium chloride, = ·4757 grm. of ammonia;

VIII. ·9870 grm. of (*c*) gave, with hydrochloric acid, ·5427 grm. of carbonic anhydride to soda-lime;

IX. ·9490 grm. of (*c*) neutralized a volume of standard sulphuric acid, equivalent to ·3137 grm. of ammonia:

A sample labelled "commercial," indistinctly crystalline, of the rose-tint, often seen in carbonate made from gas-liquor:—

X. 1·4635 grms. neutralized a volume of standard sulphuric acid, equivalent to ·4663 grm. of ammonia;

XI. 1·0574 grms. yielded, with hydrochloric acid, ·5775 grm. of carbonic anhydride to soda-lime:

A sample purchased from the same firm as the last, but labelled "pure," identical in appearance with the last:—

XII. 1·5314 grms. neutralized a volume of standard sulphuric acid, equivalent to ·4888 grm. of ammonia:

A sample in sealed bottle, labelled "from volcanic ammonia," beautifully crystalline and translucent, devoid of colour, in thinner cakes than usual:—

XIII. ·9855 grm. neutralized a volume of standard sulphuric acid, equivalent to ·3230 grm. of ammonia;

XIV. ·9790 grm. neutralized a volume of standard sulphuric acid, equivalent to ·3205 grm. of ammonia:

A sample, labelled "optim," from a wholesale druggist's, not very crystalline, devoid of colour:—

XV. 1·0704 grms. neutralized a volume of standard sulphuric acid, equivalent to ·3392 grm. of ammonia:

A sample, purchased from the same firm as the last, labelled with a well-known maker's name, in two closely-adherent layers, of which one (*a*) was about twice as thick as the other, indis-

tinctly crystalline, with conchoïdal fracture, and the other and thinner layer (*b*) highly crystalline :—

XVI. 1·0261 grms. of (*a*) neutralized a volume of standard sulphuric acid, equivalent to ·3230 grm. of ammonia ;

XVII. ·9667 grm. neutralized a solution of standard sulphuric acid, equivalent to ·2188 grm. of ammonia ;

XVIII. 1·0443 grms. gave, with hydrochloric acid, ·5785 grm. of carbonic anhydride to soda-lime, and ·7250 grm. of ammonium chloride, = ·2306 grm. of ammonia.

These results, calculated for parts per cent., give the following numbers :—

		Carb. anhyd.		Amm.
a	I	54·86		—
	II	—		32·61
	III	—		32·74
	IV	—		32·48
b	V	55·24		—
	VI	—		32·91
	VII	—		33·02
c	VIII	54·98		—
	IX	—		33·05
	X	—		31·65
	XI	54·62		—
	XII	—		31·92
	XIII	—		32·78
	XIV	—		32·73
	XV	—		31·68
	XVI	—		31·48

(The calculated numbers for the results of the analyses XVII and XVIII, are entirely different from the others, and will be given and discussed presently.)

These numbers agree in the closest manner with the theoretical numbers, except that the presence of 1 or 2 per cent. more water is indicated than is required by the formula. Here are the calculated numbers for a compound of the formula,

$$(CO_2)_2OH_2(NH_3)_3,$$

—(1) when pure, and (2) when containing 2·5 per cent. additional water (= $\frac{1}{4}OH_2$) :—

	(1.)	(2.)
Carbonic anhydride	56.05	54·65
Ammonia	32·48	31·67
Water	11·47	11·18
Additional water	—	2·50
	100·00	100·00

It will be seen, by comparing the numbers deduced from my analyses with these numbers, that all the samples examined had a composition lying between that of the pure compound, and one with 2·5 per cent. additional water. Another slight variation is, however, observable, namely, that the ammonia very slightly exceeds the calculated quantity—in the extreme cases to the extent of about 1 per cent. But it will be seen that these variations from the calculated composition are immaterial so far as the determination of the atomic composition is concerned. When treating of the products of the distillations yielding carbonates of ammonia, and of the formation of the commercial carbonate, I shall have again to refer to these variations. I shall also have then to point out that a compound of the composition I find the carbonate of commerce to possess, is the commonest among these products of distillation. Rose also obtained and described carbonates having more nearly this composition than any other. For one of these he deduced the atomic composition expressed by the formula

$$(CO_2)_5(OH_2)_4(NH_3)_8.$$

The sample to which he gave this formula yielded him numbers which correspond very closely with those calculated for a compound of the formula

$$(CO_2)_2OH_2(NH_3)_3$$

with 5 per cent. of additional water (= nearly $\frac{1}{2}OH_2$). Here are the calculations for the two formulæ, and the numbers obtained:—

		Calculation.	
	Expt.	Rose's form.	
Carbonic anhydride ..	52·92	51·38	53·25
Ammonia	31·13	31·85	30·86
Water	—	16·77	10·89
Additional water	—	—	5·00
	100·00	100·00	100·00

Other samples examined by him he considered to be intermediate in composition between this compound and the old commercial salt. His examination of these was incomplete, but the numbers he obtained suggest to me the formula I attribute to carbonate now in commerce with a variable quantity of additional water. All these products he obtained by distilling the commercial carbonate of the old composition. By distilling the half-acid carbonate which crystallises from solution, he obtained a product which agrees much more closely with my formula for the carbonate at present in commerce, with 10 per cent. additional water (= nearly $10H_2$), than with his formula—

$$(CO_2)_5(OH_2)_5(NH_3)_8,$$

as the following table shows:—

	Expt.		Calculation.	
			Rose's form.	
Carbonic anhydride ..	50·46	51·65	49·32	50·45
Ammonia	29·86		30·61	29·23
Water.....	—		20·07	10·32
Additional water	—		—	10·00
			100·00	100·00

Lastly, he obtained another compound from a residue from the distillation of one of the carbonates, and gave it the formula—

$$(CO_2)_5(OH_2)_{12}(NH_3)_8.$$

and this compound also yielded numbers corresponding much more closely to those indicating the commercial carbonate of the present time, associated with about 30 per cent. of water (= about $3\frac{3}{4}$ OH_2), than with those of the formula given to it by him, as the following table shows:—

	Expt.		Calculation.	
			Rose's form.	
Carbonic anhydride ..	38·31	40·73	38·50	39·23
Ammonia	22·70		23·90	22·74
Water.....	—		37·60	8·03
Additional water	—		—	30·00
			100·00	100·00

The analysis of the commercial carbonate made by Ure in 1817 corresponds much better with the composition I find the carbonate at present to have, together with 4 per cent. additional water (= about $\frac{1}{3}OH_2$), than with the other formula, thus:—

	Expt.	$(CO_3)_3(OH_2)_2(NH_3)_4$.	$(CO_3)_2OH_2(NH_3)_3$. With 4 per cent. of water.
Carbonic anhydride..	54·5	55·9	53·8
Ammonia	30·5	28·8	31·2
Water	—	15·3	15·0
		100·0	100·0

The analysis made by Phillips, and one by Rose, of the commercial carbonate, yielded results indicating a composition intermediate to those represented by the two formulæ.

It is of some interest to adduce proofs, other than analytical, that the carbonate now in commerce differs from that most generally in commerce formerly. Firstly, Rose found on distilling the ordinary commercial carbonate at a very gentle heat that the contents of the retort gradually liquefied. I have repeated his experiment, with the utmost care to proceed as slowly as possible, taking, for instance, about 90 hours' continuous and nearly uniform heating to distil about 250 grms., and obtained hardly any liquid at all: yet the products of distillation were less hydrated than those he obtained.

Secondly, as I have already pointed out, by distilling the carbonate at present in commerce with anhydrous calcium, chloride, ammonium carbamate condenses. Now this allows of no explanation, unless the carbonate is admitted to have a different composition from what it used to have. The reactions in the two cases are expressed by the following equations:—

$$2(CO_2)_2OH_2(NH_3)_3 + 2CaCl_2 = 4NH_4Cl + 2CO_3Ca + \overbrace{CO_2 + 2NH_3}^{\text{To form carbamate.}}$$

$$(CO_2)_3(OH_2)_2(NH_3)_4 + 2CaCl_2 = 4NH_4Cl + 2CO_3Ca + CO_2$$

Thirdly, as shown by a trial described further on, the commercial carbonate loses by exposure a proportion of its weight corresponding closely with that calculated, as due to carbamate, from the formula deduced from my analyses.

Fourthly, its solubility is about twice as great as that of

acid carbonate, of which it contains about half its weight, according to the formula I have deduced for it.

Fifthly, its saturated solution does not seem as if it were charged with carbonic anhydride, as does that of the half-acid ammonium carbonate.

Commercial Acid Carbonate.—I have stated that I have found one special exception to the uniformity in composition of the commercial carbonate. This occurred in a crystalline layer intimately united to a barely crystalline layer of the ordinary composition. I have already given the results of my analyses of this layer of exceptional composition. Calculated into parts per cent. they give numbers nearly identical with those of the acid carbonate. This layer differed from the other, and the ordinary carbonate, in having scarcely any smell or any ammoniacal taste; in dissolving only slowly in the mouth; and in not losing its translucency by exposure to the air. The occurrence of the acid carbonate in commerce must be very rare, because its difference from the ordinary carbonate is so striking and such as to render it valueless for most of the purposes of pharmacy and medicine for which it is required. So far as I am aware, this occurrence has only once before been pointed out, and this was done nearly fifty years ago by Phillips,* who published his analysis of a sample which Henry and himself had examined. Like the sample I have examined, this was more crystalline than usual. It must not, therefore, be concluded, however, that the acid carbonate in this form is essentially more crystalline than the ordinary carbonate of commerce; for this is often sent out by the manufacturer much more crystalline than the layer of the acid carbonate I have described. It was adherent to about twice its weight of the ordinary commercial carbonate, so that the cake as a whole had, therefore, the mean composition indicated for it by the "British Pharmacopœia." Thus:—

	Atomic wts.		Parts.
Commer. carb. .. $(CO_2)_2OH_2(NH_3)_3$	157	or	2
Acid carbonate.....	79	or	1
Ammoniæ carbonas, B.P. $(CO_2)_3(OH_2)_2(NH_3)_4$..	236	or	3

* On the Bicarbonate of Ammonia. Annals of Philosophy, vol. xvii, p. 110.

Whether this circumstance was accidental or intentional on the part of the maker I cannot say.

The details of the analysis of this layer of acid carbonate have already been given. I have reserved till now giving the calculated numbers per cent. With them I place those of Phillips.

	Calc.	XVII.	XVIII.	Phillips.
Carbonic anhydride ..	55·70	—	55·40	55·5
Ammonia	21·52	22·63	22·08	21·16
Water.....	22·78	—	—	
	100·00			

The acid carbonate, it will be remembered, can easily be obtained in the above form by distilling the ordinary form of it very slowly.

In the remarks which follow on the commercial carbonate it is to be understood that the usual variety only is referred to.

Behaviour on Exposure.—Two clean lumps of the compact carbonate, the analysis of a sample of which is numbered XII in the list given a few pages back, weighing together 25 grms., were exposed for some weeks at a mean temperature of about 10° C., and then weighed. They were found to have lost nearly 11 grms. in weight; they were opaque, but they still preserved their shape and size. They could be lightly handled without soiling the fingers, and squeezed pretty firmly without being crushed. They were found to be fully changed to their centre. Their loss corresponded to 43 or 44 per cent. This nearly agrees with the calculated loss, which is about 42 per cent., if the amount of acid carbonate in the sample be approximately estimated by the quantity of water in it, according to the tables at the top of p. 236. The calculated loss by exposure of the carbonate formerly in commerce of the formula $(CO_3)_3(OH_2)_2(NH_3)_4$ is only 33 per cent. A sample of commercial carbonate lost by 24 hours' exposure, according to Dalton, 50 per cent. of its weight; this makes it probable that it had the composition I find the carbonate to have at present, for when free from any water in addition to that in the formula, this is just its calculated loss by exposure. In cold moist weather the commercial carbonate appears to be slightly deliquescent, but in consequence of other changes it is difficult to decide this point conclusively.

Behaviour when Heated.—The commercial carbonate gets moist

when heated; it is, of course, gradually dissipated. The products of its distillation will be afterwards described.

Behaviour with Water.—It dissolves in four parts of water at 15°, according to my experiments. Perfectly clean lumps were weighed and dropped into a weighed quantity of water (fresh boiled and cold) in a stoppered bottle; the bottle was kept in a place at a temperature always very near 15°, and was often agitated. In different experiments varying proportions were used. On cooling slightly the saturated solution it deposited crystals of acid carbonate. Cooled in ice the deposit of crystals was still more copious, and consisted always of acid carbonate; although it has been stated* that the half-acid carbonate then crystallizes out.

The ordinary method of determining solubilities cannot, it is evident, be employed in this case, because a saturated solution decomposes any fresh carbonate added to it.

As above determined, its solubility accords with that of the acid carbonate it contains, namely, about half its weight. The solubility of the carbonate which used to be in commerce has been variously stated as lying between that of 1 in 2 of water, and 1 in 4 of water. I think it must have been less than this, as that carbonate contained about two-thirds of its weight of acid carbonate, and ought, therefore, to have had on this mode of estimation a solubility of only 1 in 5. In support of this belief I may here recall the fact that the solubility of the half-acid ammonium carbonate, as determined by me, seems to be directly dependent upon that of the acid carbonate contained in it.

A saturated solution, unlike one of the acid carbonate, or of the half-acid carbonate, does not act like a saturated solution of carbonic anhydride. The strongest hot solution I have been able to make is that of 1 in $1\frac{1}{2}$ of water. This was made by dropping this proportion of the carbonate, crushed small, suddenly into the hot water contained in a wide-mouthed bottle fitted with a caoutchouc stopper, then closing the bottle and keeping it hot in the water bath; I have no record of the temperature. Only a little carbonic anhydride was lost, unless the water was near the boiling point, and the salt added to it gradually. When made, the stopper of the bottle containing it could be withdrawn without anything more than a very slight escape of bubbles; so that from other experiments I believe the

* Pelouze et Frémy. Traité de Chimie, vol. ii, p. 483 (1861).

temperature to have been about 65° C. The old carbonate of commerce is stated in Berzelius's "Lehrbuch"* to be soluble in twice its weight of water at 49° C.

A cold saturated solution of the old carbonate was stated by Griffiths† to boil at a temperature of 82° C. John Davy found such a solution to decompose at a lower temperature than this, bubbles beginning to appear at 49° C. I have tested the modern carbonate, and find a solution of it of 1 in 4 begins to effervesce, though only slightly, at 60° C., effervesces copiously at 75°, and continues to do so as the temperature rises, which it does rapidly. At 85°, or a little below, the products of effervescence, which before consisted almost entirely of carbonic anhydride, contain much ammonia, and begin to condense on the neck of the flask or retort. At 100° C. the solution has given off all the carbonate it contained, and is nothing but water (Griffiths). I have just stated that the cold saturated solution differs from the saturated solution of half-acid carbonate, in not behaving like a saturated solution of carbonic anhydride; and there can be no doubt that this fact, and that of the point of incipient effervescence in the two solutions when heated being different, are due in part to the difference in the ratio of the ammonia to the carbonic anhydride in them. The following experiment shows the effect of dilution upon the production of effervescence. Some of the same solution as that used in the previous experiment was mixed before heating with an equal bulk of water (freshly boiled and cooled), and then did not begin to effervesce until about 70° C., was only in full effervescence at 80° C. or higher, and only at 90° C. began to yield products of effervescence which condensed in the neck of the flask. In both these experiments the heat was applied by a water-bath. Griffiths' statement must not be supposed to be so much at variance with that of J. Davy as the latter seemed to consider it; for Griffiths meant apparently by the boiling-point of this solution the point at which the products of the effervescence begin to be such as undergo condensation, and this would probably occur with the old carbonate at about 82° C.

The action of a saturated solution upon more commercial carbonate is well known to be the production of a sort of skeleton

* Vol. iii, p. 313.

† Quarterly Journal of Science (1825), vol. xviii, p. 91. On the Boiling-points of Saturated Solutions.

of the pieces of carbonate, consisting of the acid carbonate. I have only to add that by prolonged digestion I have found the particles of this mealy skeleton to grow into, or be replaced by, transparent crystals of the same substance.

I have examined the effects of heating the commercial carbonate with a little water, and have found that bubbles of carbonic anhydride escape through the solution from the undissolved lumps at a lower temperature than they escape from a cold saturated solution heated alone. Thus, from about 40°—45° C. very slight effervescence was visible, due probably to an escape of the air entangled in the pores of the carbonate. At 47° decided effervescence commenced; this became copious at from 54°—56°, and at this temperature crystals began to form in the neck of the flask. (In this and the preceding experiments the mouth of the flask, as I should have mentioned before, was loosely closed so as to prevent diffusion of the vapours given off.) Cooled down to 51° the escape of bubbles ceased. Heated again and kept at from 56°—60° effervescence went on again, the condensation of the vapours appeared to be complete, and the lumps which had originally been barely covered with water disappeared entirely in a couple of hours. During their solution they seemed to dissolve entire, for no temporary residue of acid carbonate or any loss of translucency in the lumps was seen. The products of the distillation were examined, and the results of the examination will be found among those of the examination of the products of distillation. The solution on cooling deposited crystals first of acid carbonate, and then of half-acid carbonate, determined to be such by their form. The mother-liquor was a very concentrated solution of normal carbonate, with a very little acid carbonate. Tested for carbamate the result was negative. A modification of this treatment of water with the commercial carbonate has been several times referred to in this paper, and it only remains now to give some details by which the nature of the reaction will be more fully illustrated.

Here are the details of one of my experiments. A large flask with short neck, fitted with a caoutchouc stopper, was employed for making the solutions. This stopper was only used to prevent diffusion, and was loosened at times to allow for expansion and contraction of air, and evolution and absorption of carbonic anhydride. The flask was heated over a water-bath, and the

carbonate dissolved at a sufficiently low temperature to avoid more than occasional and trifling effervescence. (Were the object merely to get the normal carbonate, it would be desirable rather than otherwise to encourage this effervescence in the earlier stages.) In the later stages of the experiment the solution could be heated much higher than at first without effervescence ensuing. As the carbonate otherwise dissolved slowly, it was crushed nearly to powder before being added, and after its addition the flask was frequently agitated. The lumps of carbonate, before they were crushed, were well scraped, so as to remove superficial acid-carbonate. The crops of crystals were drained in the flask as far as possible, then thrown on a muslin filter, and as much as possible of the mother-liquor pressed out and added to the rest.

I started with 28 parts of water; in this I dissolved by heat 11 of carbonate; next day, the weather being very cold and the flask having been out in the open air, a good crop of crystals had formed: they were acid carbonate. The mother-liquor weighed 35·2 parts; in this 5·5 parts of carbonate were dissolved. Next day, under circumstances like the last, more crystals of acid carbonate had formed. The mother-liquor weighed 36·8 parts; in this 4 parts of carbonate were dissolved. Next day more crystals of acid-carbonate had formed. The mother-liquor weighed 37·4; in this 4 parts of carbonate were dissolved. Next day more crystals of acid-carbonate had separated. The mother-liquor weighed 34·3; in this 5 parts of carbonate were dissolved. Next day crystals had formed, which were either acid-carbonate or half-acid carbonate; the record of my experiment is here imperfect. The mother-liquor weighed 30 parts; in this 3 parts of carbonate were dissolved. Next day crystals of half-acid carbonate had separated. The mother-liquor weighed 27·8 parts; in this 4 parts of carbonate were dissolved. Next day more crystals of half-acid carbonate had separated. The mother-liquor weighed 24·6 parts; in this 4 parts of carbonate were dissolved. Next day more crystals of half-acid carbonate had separated. The mother-liquor weighed 20·9 parts; in this 3·5 parts of carbonate were dissolved. Next day more crystals of half-acid carbonate had separated, together with a few crystals of normal carbonate. The mother-liquor weighed 17·8 parts; set aside, it yielded in a few days a quantity of crystals of normal carbonate. The total quantity of commercial carbonate thus passed in solution

through the water was therefore about $1\frac{1}{2}$ times its weight. But for the unavoidable loss of mother-liquor with each batch of crystals, probably $\frac{1}{2}$ part more would have been used.

When the mother-liquors are tested after one or two crystallizations of half-acid carbonate, they are found to contain caustic ammonia after all carbonate has been removed by calcium chloride. This fact I have verified repeatedly and most carefully. These mother-liquors smell powerfully of ammonia, and are very concentrated solutions of carbonate and carbamate. They generally refuse to mix with rectified spirit. If after shaking two layers form, the lower aqueous one soon solidifies into a crystalline mass, while the upper spirituous layer becomes also filled, but only slowly, with crystals. The crystals are half-acid and acid carbonates, and the remaining mother-liquor is very ammoniacal. With ammonia gas the mother-liquors (original) yield much normal carbonate and solutions still concentrated; a fact which shows that the mother-liquor contains a great deal of carbamate, as the normal carbonate is only sparingly soluble in presence of much ammonia. After this treatment with ammonia, the mother-liquors yield with a concentrated solution of calcium chloride in excess more or less soluble precipitates, which are either calcium carbamate, or carbonate of ammonium and calcium, as I have established in a previous section of this paper. By standing in closed vessels the mother-liquors usually yield crystals, which continue to grow for some time, of either the half-acid carbonate or, more usually, the normal carbonate. The following are the particulars of some analyses I made of these mother-liquors, with a view of determining approximately their strength:—

1 c.c. neutralized a volume of standard sulphuric acid equivalent to ·2193 grm. of ammonia = ·5631 grm. of ammonium carbamate, or ·7353 grm. of normal ammonium carbonate.

1 c.c. of the same mother-liquor neutralized acid corresponding to ·2159 grm. of ammonia = ·4953 of carbamate = ·7239 grm. of carbonate.

1 c.c. of a mother-liquor from another experiment neutralized acid equivalent to ·1683 grm. of ammonia.

[On adding rectified spirit in small quantity to this mother-liquor I obtained a crystalline precipitate, which I could not get perfectly dry. On analysis it gave numbers corresponding to a half-acid carbonate with from 8 to 10 atoms of total water

$(CO_2)_3(OH_2)_8(NH_3)_4$, or $(CO_3)_3(NH_4)_4H_2,(OH_2)_5$.

Exposed to the air it became a wet mass of acid carbonate. I may here recall the fact that Rose once obtained from the fluid residue of the distillation of one of the carbonates described by him a mass of minute crystals of the composition represented, according to him, by the formula—

$$(CO_2)_5(OH_2)_{12}(NH_3)_8,$$

or, according to me (p. 238), by the formula—

$$(CO_2)_2(OH_2)_5(NH_3)_3.$$

His and my observations, taken together, render probable the existence of one or more highly hydrated carbonates depositing from solutions.]

·5 c.c. of another mother-liquor, which had deposited a good deal of normal carbonate, yielded ·1207 grm. of carbonic anhydride.

·5 c.c. of the same neutralized acid = ·0961 grm. of ammonia. These numbers correspond to the ratio of 113 atoms of ammonia to 54·9 atoms of carbonic anhydride.

[This mother-liquor was the one that, after treatment with ammonia, yielded with calcium chloride the soluble precipitate of either double carbonate of ammonium and calcium, or of calcium carbamate.]

The reactions by which water and the commercial carbonate are made to yield the acid, half-acid, and normal meta-carbonates of ammonium, and a solution of ammonium carbamate, and of either ammonia or normal ammonium orthocarbonate or ammonium orthocarbamate, may be represented as follows :—

1st stage. $(CO_2)_2OH_2(NH_3)_3 = \underset{\text{Acid carbonate crystals.}}{CO_2OH_2NH_3} + \underset{\text{Carbamate in solution.}}{CO_2(NH_3)_2}$.

2nd „ $\underset{\text{In solution.}}{CO_2(NH_3)_2} + 2OH_2 = \underset{\text{Norm. carbonate in solution.}}{CO_2(OH_2)_2(NH_3)_2}$.

3rd „ $2(CO_2)_2OH_2(NH_3)_3 + \underset{\text{In solution.}}{CO_2(OH_2)_2(NH_3)_2} =$

$$\underset{\text{Half-acid carbonate crystals.}}{(CO_2)_3(OH_2)_4(NH_3)_4} + 2\underset{\text{Carbamate in solution.}}{CO_2(NH_3)_2}$$

In solution. Normal carbonate in crystals.

4th stage. $CO_2(NH_3)_2 + 2OH_2 = CO_2(OH_2)_2(NH_3)_2$.

5th „ $3(CO_2)(OH_2)_2(NH_3)_2 = (CO_2)_3(OH_2)_4(NH_3)_4 + 2NH_3 + 2OH_2$,

or, $4(CO_2)(OH_2)_2(NH_3)_2 = (CO_2)_3(OH_2)_4(NH_3)_4 +$

Normal orthocarbonate.

$CO_2(OH_2)_2(NH_3)_4 + 2OH_2$,

or, $4CO_2(NH_3)_2 + 4OH_2 = (CO_2)_3(OH_2)_4(NH_3)_4 +$

Orthocarbamate.

$CO_2(NH_3)_4$.

Behaviour with Alcohol.—It is well known that rectified spirit dissolves out carbamate from the commercial carbonate, leaving undissolved the acid carbonate.

Hünefeld,* in 1836, heated the commercial carbonate with spirit of 90 per cent., and found that at 47°·5 C. some bubbles began to rise from the lumps, that this phenomenon became quite evident at 50°, and that from 56° to 62° there was copious effervescence of nothing but carbonic anhydride. Above this temperature the gases escaping condensed in the neck of the retort as a neutral compound, and the distillate which now formed was a neutral solution. I have repeated the experiment of heating the carbonate at present in commerce with spirit of about 90 per cent., with somewhat modified results. Of the products of distillation I shall say nothing at present. Minute bubbles began to escape from the lumps at 41°; at 45° there was very evident effervescence from the lumps; at 50° there was copious effervescence with a simmering noise; at 51° the products of the effervescence began to condense; while at 53° the effervescence was exceedingly great. The temperatures observed by me as marking the stages of this phenomenon are, therefore, lower than those observed by Hünefeld. The heat was applied by means of a water-bath, and the flask was loosely closed by a caoutchouc stopper to prevent diffusion. On keeping the spirit for some hours at 52°, effervescence continued, and there was little or no loss of spirit; at the end of the operation the neck of the flask had become only thinly encrusted with the products of the effervescence, and the car-

* Journ. für prakt. Chemie, vol. vii, p. 25.

bonate had only partly dissolved. The lumps on removal appeared externally to be but little altered in structure. Internally, too, they were unchanged; for fragments yielded on analysis 54·51 per cent. of carbonic anhydride, and 32·22 per cent. of ammonia. The spirit proved to be a little weaker than before, dry pearl-ash separating a little water. It contained a little ammonium carbamate, still less ammonium carbonate, and a marked though small quantity of ammonia. Left at a temperature of about 0° for two days, it did not crystallise.

Behaviour with Ammonia.—Concentrated ammonia-water in the cold dissolves out carbamate, and converts the acid carbonate into normal carbonate, either by removing half its carbonic anhydride, or by combining with it and an atom of water. On cooling a mixture of commercial carbonate in powder with four times its weight of the strongest commercial solution of ammonia soon after it was made, only indistinct evidence was given of the formation of the minute crystals observed under similar circumstances when the acid carbonate is used. The commercial carbonate digested at 20°—25° in a closed vessel with a saturated solution of ammonia, as already described in the case of the normal and acid carbonates, slowly dissolves in apparently unlimited quantity, and the solution deposits on cooling crystals of ammonium carbamate, and a very little normal carbonate. The reaction may be thus represented:—

$$(CO_2)_2OH_2(NH_3)_3 + NH_3 = 2CO_2(NH_3)_2 + OH_2.$$

Behaviour when Heated with Anhydrous Potassium Carbonate.—As already described the gases evolved condense to carbamate, ammonia escaping, according to this equation:

$$(CO_2)_2OH_2(NH_3)_3 + CO_3K_2 = 2CO_3KH + \overbrace{CO_2 + 2NH_3}^{\text{Forming carbamate.}} + NH_3.$$

The contents of the retort have been found, in accordance with this equation, to be more or less completely acid potassium carbonate. For a short time after the mixture is made, ammonia is evolved in very small quantity at ordinary temperatures, and escapes in bubbles through the mercury into which the beak of the retort is made to dip, but this is probably due to the presence of a little moisture. It is only at from 50° to 60° that a material reaction is set up; and here a phenomenon presents

itself which is of considerable interest. Nothing but ammonia is given off, and by maintaining the heat at 60°, this evolution of ammonia can be nearly or quite terminated before any carbamate-forming gases come off. It is not until the temperature is carried to 65°, that the formation of carbamate begins, and not until it is carried on towards and up to 80° that the whole of the carbamate is obtained. Hence the reaction occurs distinctly in two stages, according to the following equations :—

1st stage: $(CO_2)_2OH_2(NH_3)_3 + CO_3K_2$
$= NH_3 + CO_2(NH_3)_2,2CO_3KH.$
or $= NH_3 + CO_2(NH_3)_2,CO_3KH + CO_3KH.$

2nd stage: $CO_2(NH_3)_2,CO_3KH = \underbrace{CO_2 + 2NH_3}_{\text{To form carbamate.}} + CO_3KH.$

Further proof of a union of the acid potassium carbonate with ammonium carbamate is afforded by the facts that on distilling the commercial carbonate with calcium chloride, the components of the carbamate are driven off at a temperature of 52°—65°, and that on heating carbamate alone, it is converted into vapour at 59° or 60°; whereas in the present case the carbamate is not formed until the temperature reaches 65°, and passes on to 80°. The special interest of this point is its bearing on the difficult question as to whether the commercial 'carbonate of ammonia' is a double salt or only a mixture of salts.

Behaviour when Heated with Anhydrous Calcium Chloride.—At a temperature of 50°—52°, the mixture evolves gases, a part of which condenses as carbamate, that escaping being carbonic anhydride; from this temperature up to 60° or so, the reaction goes on steadily, but the escape of carbonic anhydride greatly diminishes; how far the rate of formation of carbamate also slackens I have had no means of determining. The residue in the retort consists of unchanged anhydrous calcium chloride, of calcium carbonate, and ammonium chloride. The reaction may be thus expressed in symbols :—

$$2(CO_2)_2OH_2(NH_3)_3 + 2CaCl_2 = 2CO_3Ca + 4NH_4Cl + \overbrace{\underbrace{CO_2 + 2NH_3}_{\text{To form carbamate.}}} + CO_2.$$

The carbonate of the composition—

$$(CO_3)_3(OH_2)_2(NH_3)_4,$$

must fail to yield carbamate in this way, because there is enough water in it to convert all the ammonia into ammonium. It cannot be admitted, as might on first thought be imagined, that the calcium chloride may simply remove the water to form a hydrated calcium chloride; for were it to do so, the hydrated chloride would react with the carbamate to form calcium carbonate and ammonium chloride. This is proved by the experiment described in the next paragraph.

When solid calcium chloride, with about 2 atoms of water, is mixed in coarse powder with the commercial carbonate, the smell of ammonia entirely disappears; and soon after the mixture has been made it gets warm, swells up considerably, and evolves quantities of carbonic anhydride. When the action is over, on heating the mass to 50° or above, more carbonic anhydride is evolved. I happened in one case to be so fortunate as to mix the two in equivalent proportions. The consequence was that nothing was given off but carbonic anhydride and water. The residue was a porous mass of ammonium chloride and calcium carbonate. Treated with water, a solution was obtained which gave a faint precipitate with solution of ammonium carbonate and ammonia, and on the other hand a faint opalescence with calcium chloride. The insoluble matter was calcium carbonate. By using an excess of the carbonate of commerce, along with the carbonic anhydride and the water, the constituents of the excess of the carbonate escape. Mixed with common salt, the carbonate is, I believe, partly converted into sodium carbonate and ammonium chloride when treated with a little water, but I have no experience of the fact. In the dry state no reaction seems to take place, no gas being evolved and the smell of ammonia remaining undiminished.

Chemical Constitution.— The discussion of the question as to whether the commercial carbonate is a single substance or a mixture I must reserve until I have treated of the products of distillations yielding compounds of carbonic anhydride, water, and ammonia. The weight of evidence is, I think, decidedly in favour of its being a single substance—that is, of the carbonate at present in commerce, not the old carbonate, being so.

Regarded as a single substance, its constitution seems to be

simple enough. It is that of a double salt of carbonic and carbamic acids, as is shown by the formula—

$$CO_3NH_4H,C(NH_2)O_2NH_4,$$

or, quite as probably, by double this, or,

$$(CO_3NH_4H)_2[C(NH_2)O_2NH_4]_2.$$

Many of its reactions support the notion that it is either a mixture or a compound of carbamate and acid carbonate; they are too well known to be enumerated. None of its reactions are opposed to this notion. Another argument in favour of this view of its constitution is afforded by the fact just now referred to, that the acid potassium carbonate prevents the dissipation of ammonium carbamate by a heat of 60°, this being in all probability due to its forming a double salt with the carbamate, similar in constitution to the commercial 'carbonate of ammonia.'

The carbonate formerly so general in commerce cannot apparently be represented, assuming it to be a single substance, as of a very intelligible constitution, inasmuch as this must be that of a double salt formed of two atoms of a salt of a dibasic acid and one atom of a salt of a monobasic acid, thus:—

$$(CO_3NH_4H)_2,C(NH_2)O_2NH_4.$$

But the grounds which lead me to consider the carbonate at present in commerce as probably a single substance, cause me to regard the old carbonate as a mixture only of this with acid carbonate.

Products of the distillation of Sal-Ammoniac with Chalk, with Potassium Carbonate, and with Sodium Carbonate.

Sal-Ammoniac with Chalk.—I have already stated the collective evidence showing that when ammonium carbamate is volatilized it is not converted into vapour of itself, but into a mixture of carbonic anhydride and ammonia. In the case of the carbonates of ammonium, the evidence of their decomposition into these gases and water when heated is still more conclusive, as some water is always obtained in the free state. The nature, therefore, of the products obtained by distilling a mixture of sal-ammoniac and chalk depends upon the behaviour of a mixture of water

vapour, and ammonia and carbonic anhydride gases; or, to go a step further, as these substances do not combine with each other until their temperature is much below the condensing point of steam, and that, therefore, much of the water separates from the mixture in the liquid state, the nature of the products depends upon the reaction of equivalent quantities of moist carbonic anhydride and ammonia, and the behaviour of the product of this reaction with liquid water.

It is always stated that the products of the distillation of sal-ammoniac and chalk are the substance

$$(CO_3)_3(OH_2)_2(NH_3)_4,$$

water, and ammonia gas; but I am not aware of the publication of any investigations on which this statement rests.

It would naturally be made on theoretical considerations, based on the ascertained composition of the carbonate as it appeared in commerce. All my own experiments on the subject, direct and indirect, prove it to be incorrect; but as I have not the evidence of any manufacturer on the subject, I cannot say positively that, worked on the large scale, the distillation does not yield these products. At the same time, as I have imitated as closely as possible on a small scale the process said to be employed on the large scale, and have not got the stated result, and as I also know from a visit made some years ago to one of the largest chemical works, before this subject had any special interest for me, that the phenomena on the large scale appear like those I have observed in my own experiments, I am almost fully convinced that this statement is an incorrect one, and has been advanced upon theoretical grounds only.

When sal-ammoniac and chalk are mixed together, no reaction ensues until the mixture is considerably heated. Indeed, as I have already described, a carbonate of ammonium mixed with calcium chloride in the solid state is converted into a mixture of sal-ammoniac and chalk. It was on a mixture thus obtained I first experimented. By heating together some calcium chloride and a slight excess of the commercial carbonate of ammonia, and drying the residue in an oven, a porous and intimate mixture is obtained of sal-ammoniac and chalk in equivalent proportions, plus a small quantity in excess of chalk produced from any lime previously combined with the calcium

chloride. This mixture seemed to me well adapted for experimenting upon.

A quantity of it was packed in a cast-iron retort, connected with a series of short wide glass tubes. The last tube was narrower than the others, and its extremity was drawn out so as to leave only a small aperture. This drawn-out extremity passed into a large flask nearly air-tight. This part of the arrangement was intended to prevent free diffusion of the ammonia, without offering any obstacle to its escape by its own elasticity. The retort was then heated until vapours passed into the condensing tubes, by which time the retort had become partly dull-red hot. After a time, moist paper was wrapped round the glass vessel nearest the retort, to aid the condensation; otherwise, no special means were adopted for keeping the condensers cool. When the vapours first mixed with the air in the receivers a cloud was formed, but this soon disappeared. The products of the distillation first deposited liquid (water), then along with this a white solid. During the operation *no ammonia escaped.* An odour, but only a slight one, of ammonia was perceived by smelling at the loosely closed mouth of the flask, mixed with a more marked empyreumatic one. A good deal of liquid trickled along the floor of the receivers, but much of it crystallised before it reached the flask. When the distillation was complete, the parts of the apparatus were separated. The deposit in the several receivers or condenser-tubes was removed with as great despatch as possible, and placed in stoppered bottles, the parts of the deposit on the roof or upper side of the tubes being kept distinct from the parts on the floor. The lower parts of the deposit were slightly discoloured, and much thicker than the upper parts, consisting largely of the matter which crystallised from the liquid distillate as it trickled along. The deposit was all saturated with liquid, and did not resemble the carbonate of commerce. The small quantity of liquid which did not crystallise before it reached the flask did so to a considerable extent on standing. The retort was found to contain a semi-fused, vesicular mass, consisting of calcium chloride with some oxychloride. Treated with water, an insignificant quantity of chalk was left. The solution made with boiling water was alkaline, yielded a scum at its surface of calcium carbonate when exposed to the air, and, when concentrated, deposited on cooling some slender, apparently beaded,

crystals of alkaline reaction, which appeared to be calcium oxychloride. The deposit removed from the receivers became gradually dry by keeping in the bottles for two or three days by the union of the water and the solid matter. The part removed from the roof of the receivers was analysed the day after the distillation; it was still wet, but much less so than when first formed, and was confusedly crystalline. It contained no chloride.

I. 1·0583 grms. gave with hydrochloric acid ·5287 grm. of carbonic anhydride to soda-lime, and 1·3110 grms. of ammonium chloride = ·4170 grm. of ammonia.

II. ·9076 grm. neutralized a volume of standard sulphuric acid, equivalent to ·3594 grm. of ammonia.

III. ·8656 grm. gave ·4487 grm. of carbonic anhydride and 1·0630 grms. of ammonium chloride = ·3381 grm. of ammonia.

These numbers indicate a composition identical with that of the compound or mixture obtained by Rose, among the products of the distillation of the commercial carbonate at a gentle heat, viz.,

$$(CO_2)_2(OH_2)(NH_3)_4$$

as the following table shows:—

	Calc.	I.	II.	III.
Carbonic anhydride . .	50·57	49·96	—	50·18
Ammonia	39·08	39·41	39·60	39·06
Water	10·35			
	100·00			

It must not be forgotten that this was the composition of the *wet* deposit. The important point is, that the carbonic anhydride and ammonia were in equivalent proportions, instead of having the sesqui-ratio. I also wish to call attention to the fact, that it contained only 10·35 per cent. of total water, and that yet when first collected it was saturated with fluid; for from this it is practically certain that the solid deposit first formed was ammonium carbamate, notwithstanding the presence of water. Experiments that I have described in an earlier part of this paper show that carbonic anhydride and ammonia do thus unite in the presence of water,—at least in the presence of excess of ammonia, which probably only serves to impede the hydration of the carbamate. The lower part of the deposit was not

analysed in this experiment: it contained a little ammonium chloride and other impurities. It was re-distilled in a glass-retort connected with a tube dipping under mercury. From 50° to 55° ammonia gas was evolved, and some sublimate formed. Heated to 60°, when gas had ceased to come off at 55° C, more sublimate continued to form. In about thirty hours the condensing-tube was removed and replaced by another. The heat after being kept some time longer at 60°, was raised to a considerably higher temperature (85°) for a short time, and the distillation then arrested. During the distillation the contents of the retort gradually melted, and from the time of becoming fluid, continued to effervesce or boil during the distillation. A little liquid was left in the retort, which did not crystallise on standing for forty hours. It was found to contain some normal ammonium carbonate and some ammonium chloride. Of the products of this distillation only the remote part of the deposit in the first condensing-tube employed was fully analysed. The part of the deposit in this tube nearest the retort had only its ammonia determined: this corresponded to 35·23 per cent. The deposit in the second condensing-tube used had also only its ammonia determined, which corresponded to 34·67 per cent.

Of the remote part of the deposit in the first condensing-tube 1·1039 grms. gave ·5554 grm. of carbonic anhydride, and 1·1770 grms. of ammonium chloride = ·3743 grm. of ammonia.

These quantities correspond respectively to 54·78 per cent. of carbonic anhydride and 36·92 per cent. of ammonia. and therefore to a combination equivalent to that expressed by the formula $(CO_2)_4(OH_2)_{1\cdot5}(NH_3)_7$. It therefore contained more ammonia than the commercial salt and less water, including moisture or uncombined water. It was also not neutral in composition, and was equivalent to 3 atoms of carbonate, 1 atom of acid carbonate, and a little additional water. As this product was so rich in ammonia, and as some of the latter escaped during the distillation, and, further, as no ammonia escaped in the primary distillation, it may be fairly concluded that the lower impure part of the deposit in the primary distillation was, like the upper part, a neutral compound, but one containing more water, both free and combined.

O. Figuier observed,* that in distilling chalk and sal-ammo-

* Sur le carbonate d'ammoniaque ordinaire. Journal de Pharmacie, vol. xvii, p. 238.

niac no ammonia was evolved, but then he cooled his receiver by ice. He accounted for this fact by supposing that the water liberated and condensed kept the liberated ammonia in solution. But such a supposition cannot be upheld.

The result of the re-distillation of the primary product shows that this operation, also, does not yield a product of the composition of the commercial carbonate when carried on slowly. A more rapid distillation would have given a different result; and had the proportion of water in the contents of the retort been large enough—as it is stated to be made in practice by the direct addition of this substance—no doubt the commercial carbonate would have been formed, as other experiments afterwards to be described will show (p. 265).

Sal-ammoniac 1 part and chalk 2 parts, both well dried and in powder, were mixed together, reserving only a little chalk to be added afterwards. The mixture was placed in the iron retort, the remainder of the chalk spread over the top, and the distillation carried on as before. The phenomena of condensation were similar to those in the last experiment. The receiver next the retort was allowed to get warmer than in the last experiment, and the deposit in it proved to be not neutral. The remoter parts of the deposit were nearly neutral. Calcium oxychloride was found in the residue of calcium chloride and chalk. The apparatus leaked at the joint between the retort and first receiver, and through the opening, at times, ammonia-gas, mixed probably with some carbonic anhydride, rather freely escaped. The deposit in the receivers was collected as before and analysed without previous drying.

1·0863 grms. of the deposit from the roof of the first receiver neutralized acid = ·3407 grm. of ammonia, = 31·36 per cent.

1·0002 grms. gave ·4925 grm. of carbonic anhydride, = 49·24 per cent., and 1·0565 grms. of ammonium chloride = ·3360 grm. of ammonia, = 33·59 per cent.

These numbers correspond to a composition equivalent to that expressed by the formula

$$(CO_2)_4(OH_2)_{3\cdot4}(NH_3)_7.$$

The deposit from the floor of the first receiver was also analysed and found to consist of ammonia and carbonic anhydride in the same ratio as in this formula, but with considerably more water.

1·0621 grms. of the deposit from the roof of the second receiver gave ·5409 grm. of carbonic anhydride, and 1·2765 grms. of ammonium chloride, = ·4060 grm. of ammonia.

These numbers give 50·95 per cent. and 38·23 per cent. respectively, indicating a composition the same as that of the deposits in the previous distillation, or

$$(CO_2)_2(OH_2)(NH_3)_4.$$

1·4330 grms. of the very wet deposit on the floor of the second receiver gave ·6453 grm. of carbonic anhydride, = 45·03 per cent., and 1·4125 grms. of ammonium chloride, = ·4492 grm. of ammonia, = 31·80 per cent.

These numbers indicate a composition very nearly neutral, that of 6 atoms of carbonic anhydride to 11 of ammonia, and $7\frac{1}{2}$ of water.

The slightly acid character of the deposit in the first receiver in the primary distillation in this experiment, shows that with a leaky and warm receiver acid carbonate is formed. The relatively trifling amount of carbonic anhydride liberated in excess from the contents of the retort, as indicated by the alkalinity of the residue, must have very little effect on the neutrality of the products of condensation, although, according to Figuier, Dulong suggested in his lectures that to the carbonic anhydride, liberated in this way, was due the acid character of commercial carbonate. By a rough experiment, I estimated the alkalinity in this instance to be equivalent to a quantity of anhydrous lime, less than $\frac{1}{70}$ of the weight of sal-ammoniac used. The production of lime or its equivalent in this operation is certainly a secondary effect of the heat upon the calcium chloride, or calcium chloride and chalk in an aqueous atmosphere. Figuier carried on the distillation in a glass retort, and found that by applying the heat cautiously until all the ammonia was expelled, no lime or oxychloride of calcium was formed. I have also found this to be the case in another distillation of chalk and sal-ammoniac which I made.

This was done in a glass tube-retort heated in a gas-furnace, and connected air-tight to a condensing-tube dipping under mercury. Both the substances were well-dried and in fine powder. Equal weights were taken, with an additional half part of chalk filled in after the mixture. The distillation was carried on with care not to fuse the calcium chloride formed, and

arrested shortly before completion. The contents of the retort were examined and found to be neutral. The condensing-tube was then changed, and the retort again heated till its contents fused, which caused an escape of carbonic anhydride through the mercury. On removal, they were found to be markedly alkaline, and the solution of them precipitated with carbonic anhydride solution. In spite of the cautious heating and the excess of chalk, some sal-ammoniac was volatilised and condensed again in the mouth of the retort. No ammonia escaped during the distillation. The condensing-tube near the retort was cooled by a wrapping of wet bibulous paper.

The products of the distillation were a small quantity of fluid and a wet solid deposit. This was analysed in its wet state. It was exposed more than usually in the process of extracting it from the tube. The part next the retort contained some chloride. The more remote part which was analysed contained no chloride, but a trace of empyreumatic matter was present which turned brown with acid solution of silver nitrate.

·9731 grm. gave ·4700 grm. of carbonic anhydride and 1·1290 grms. of ammonium chloride = ·3591 grm. of ammonia.

These numbers correspond to 48·30 per cent. and 36·90 per cent. respectively, and indicate about a composition expressed by—

$$CO_2(OH_2)_{0\cdot8}(NH_3)_2,$$

but with less water and a little less ammonia.

These experiments are quite sufficient, I think, to show that the products of the distillation are not such as they are represented to be. The conclusion that I have come to is that the formation of the commercial carbonate takes place in the redistillation of the first obtained product, with a little water, a process like that of distilling the normal carbonate (p. 262).

Sal-ammoniac with Potassium Carbonate.—A mixture of sal-ammoniac and anhydrous potassium carbonate was distilled at a sand-heat, but the process was not completed—the upper parts not getting enough heat. Ammonia gas was evolved in the earlier part of the distillation. When first collected, the deposit was moist; it was analysed in this condition.

1·0703 grms. of the remote part gave ·5050 grm. of carbonic anhydride, and 1·1485 grms. of ammonium chloride, = ·3653 grm. of ammonia.

These numbers correspond to 47·43 per cent. and 34·31 per

cent. respectively, and indicate a composition expressed by the formula—

$$(CO_2)_8(OH_2)_{7\cdot5}(NH_3)_{15}$$

or $$CO_2OH_2(NH_3)_2,$$

with a slight excess of carbonic anhydride.

·9034 grm. of the near part of the deposit gave ·4498 grm. of carbonic anhydride and 1·0685 grms. of ammonium chloride, = ·3398 grm. of ammonia.

These numbers correspond to 49·79 per cent. and 37·61 per cent. respectively, and indicate a composition expressed by the formula—

$$CO_2(OH_2)_{\frac{3}{4}}(NH_3)_2.$$

Sal-ammoniac with Sodium Carbonate.—Stove-dried sal-ammoniac one part and fused sodium carbonate in powder one-and-a-quarter parts were mixed together, and placed in a glass tube-retort, and a quarter part more sodium carbonate added. The retort was placed in a gas-furnace, and the distillation was proceeded with as usual. Some ammonia escaped during the earlier part of the distillation. The deposit was moist, and a few drops of liquid were also obtained. It was thought unnecessary to analyse the deposit, as the experiment was only undertaken to make sure that the sodium salt acted like the potassium salt. (See p. 175 for result obtained by Rose.)

It is interesting to observe that, while in the distillation of sal-ammoniac and chalk no ammonia escapes from the cool receiver, in the distillation of sal-ammoniac and an alkaline carbonate ammonia always escapes at first. The explanation of the escape of ammonia evidently lies in the behaviour of the alkaline carbonate towards ammonium carbonate or carbonic anhydride and water. In the earlier stages some of the water and carbonic anhydride is fixed by unchanged and cool alkaline carbonate, thus:

$$CO_3K_2 + \overbrace{CO_2 + OH_2 + 2NH_3} = 2CO_3KH + 2NH_3.$$

In the later stage of the distillation this absorbed carbonic anhydride must be set free again and combine in part with some of the deposited "carbonate of ammonia."

Sal-ammoniac and Pearl-ash distilled with Aqueous Alcohol.—Some pearl-ash, with fully its equivalent of sal-ammoniac, was distilled with aqueous alcohol, according to the directions of the

London Pharmacopœia for preparing *spiritus ammoniæ aromaticus*. The first portions of the distillate soon deposited crystals in the receiver. By allowing a sufficient quantity of fluid to distil over, these crystals redissolved. The distillate, as a whole, was a solution of normal carbonate. I tested it for carbamate, but failed to get evidence of its presence. The crystals deposited by the earliest portions of the distillate were very minute; but they reminded me of crystals of the normal carbonate. On letting stand some of the earlier portions of the distillate of such a strength as only to form crystals slowly, a good quantity of very thin six-sided tables deposited, which both by their appearance and behaviour on exposure to the air, proved to be half-acid carbonate. Acid carbonate was also formed. The mother-liquor was basic, or contained more than two atoms of ammonia to one of carbonic anhydride.

The *spiritus ammoniæ aromaticus* generally proves to contain caustic ammonia, and, I think—I cannot speak with certainty, not unfrequently much less carbonate than it is intended to contain. By following the directions in the British Pharmacopœia, to use solution of ammonia and commercial carbonate instead of pearlash and sal-ammoniac, the formation of a spirit containing excess of ammonia is favoured, but to only a small extent. The spirit thus obtained is, of course, equally liable, if too strong in alcohol, to decompose into a basic solution and half-acid or acid carbonate, as I ascertained by preparing it. During the distillation crystals are apt to deposit in the neck of the retort, but they are soon dissolved again as the process goes on. The effects of distilling the commercial carbonate with aqueous alcohol and with water will be described presently.

Products of the Distillation of the Normal, the Acid and the Half-Acid Carbonates of Ammonium.

Distillation of the Normal Carbonate.—Crystals of normal carbonate in good condition, but not quite dry, were distilled in a retort heated by a water-bath. The retort was connected with a tube dipping under mercury. The heat was only kept just high enough to carry on the distillation. No means of cooling the neck of the retort or the tube were adopted. When the water-bath had a temperature of 50°, a few drops of liquid condensed in the wide part of the retort-neck, and a few needle-shaped

crystals formed on the dome of the retort. As the distillation did not proceed further at this temperature, the heat was raised very slowly, and in an hour had got to 60° without the distillation going on. At this point the contents of the retort began to liquefy, and a deposit formed in the neck of the retort. The distillation was kept going at this temperature for about 15 hours and then stopped. The product of the distillation choked the narrower part of the retort-neck. The contents of the retort were fluid. On cooling, this fluid became nearly solid by crystallization, the crystals being apparently those of the normal carbonate. Only a very little ammonia escaped during the distillation. The deposit was hard and crystalline, and almost dry. The results of its analysis have already been given, as it approaches ammonium carbamate in composition (*i*, pp. 222–3). It is, however, more exactly represented by the formula—

$$(CO_2)_4OH_2(NH_3)_8,$$

with a very slight excess of carbonic anhydride.

The fact that the deposit was moist as it formed, fully justifies the assertion that it was first pure carbamate and then became slightly hydrated. Here, then, is further proof that in distilling sal-ammoniac and chalk the first solid product that condenses is the carbamate, p. 255. (See also pp. 268, 270.)

Some crystals of normal carbonate were distilled, as in the last experiment, except that more heat was applied. The distillation was carried on at a temperature of about 65°. A good deal of ammonia escaped. The operation was arrested as before. The contents of the retort were similar to those in the last experiment. But the product of condensation was damp and not so compact, and differed in composition from the product of the previous distillation. It was crystalline.

·9478 grm. gave ·5114 grm. of carbonic anhydride and ·9875 grm. of ammonium chloride, = ·3141 grm. of ammonia.

These numbers correspond to 53·96 per cent. and 31·80 per cent. respectively, which indicate a composition like that of the carbonate of commerce—

$$(CO_2)_2OH_2(NH_3)_3,$$

with a slight excess of ammonia and with 4 per cent. of additional water, as the following comparison shows :—

	Calc.	Found.
Carbonic anhydride	53·81	53·96
Ammonia.....	31·18	31·80
Water	11·01	—
Additional water	4·00	—
	100·00	

Distillation of the Acid Carbonate.—Some acid carbonate in dry crystals was distilled at about 60° (p. 199). At 50° a few drops of fluid condensed in the neck of the retort, which gradually crystallized; but it was only at about 60° that the process of distillation went on. During the process a little carbonic anhydride must have escaped, but it happened that in this distillation the end of the long condensing tube did not dip under mercury, but, to impede diffusion, was only closed nearly air-tight. After the distillation had lasted about 70 hours, it was stopped. The contents of the retort were dry, unchanged acid carbonate. The condensed product was almost dry, crystalline and translucent, in parts almost transparent. It was removed, and different parts of it were analysed.

*a*I. ·5690 grm. of the deposit nearest the source of heat, which was thin and nearly opaque, as if from decomposition during the distillation, neutralized a volume of standard sulphuric acid equivalent to ·1343 grm. of ammonia.

*a*II. ·9627 grm. of the same yielded ·5311 grm. of carbonic anhydride.

*b*I. ·1·0600 grms. of the part of the deposit lying next to the preceding, and between this and the thick part, nearly transparent, neutralized a volume of acid equivalent to ·2346 grm. of ammonia.

*b*II. 1·2198 grms. of the same neutralized acid equivalent to ·2664 grm. of ammonia.

*b*III. 1·0069 grms. of the same gave ·5542 grm. of carbonic anhydride and ·6994 grm. of ammonium chloride = ·2224 grm. of ammonia.

*c*I. 1·0140 grms. of the remoter part of the thick crystalline deposit neutralized acid, = ·2351 grm. of ammonia.

*c*II. ·9458 grm. of the same gave ·5192 grm. of carbonic anhydride and ·6693 grm. of ammonium chloride, = ·2219 grm. of ammonia.

*c*III. 1·1203 grms. of the same neutralized acid, = ·2338 grm. of ammonia.

dI. 1·0610 grms. of the remotest part, very thin, gave ·5730 grm. of carbonic anhydride and ·7049 grm. of ammonium chloride = ·2242 grm. of ammonia.

These numbers correspond to a composition closely approaching that of the acid carbonate with a slight excess of ammonia, as the following table exhibits:—

	Carb. anhyd.	Ammonia.
a I.....	—	23·60
a II	55·17	—
b I.....	—	22·13
b II	—	21·84
b III.....	55·04	22·09
c I.....	—	23·20
c II	54·90	22·51
c III.....	—	20·86
d	54·01	21·13
Calc.	55·70	21·52

By redistilling the product of distillation having the composition equivalent to that of the carbonate now in commerce with 10 per cent. additional water, Rose obtained a deposit having nearly the composition of the acid carbonate, but with about 10 per cent. of additional water (p. 203). By distilling crystals of the acid carbonate he obtained a product having a composition which he represented by a formula which would at present be written

$$(CO_2)_7(OH_2)_{12}(NH_3)_8,$$

but which approaches much more nearly that of the acid carbonate with 12 per cent. of additional water. Here are Rose's numbers, and those calculated for this formula, along with those for the acid carbonate:—

	⅞ Carb.	Expt.		Acid Carb.
Carbonic anhydride..	46·71	47·70	48·90	49·01
Ammonia	20·71	19·41		18·94
Water.....	32·58	—		20·05
Additional water	—	—		12·00
	100·00			100·00

Some more of the acid carbonate was distilled as before, except that the heat was much higher, and that the condensing

tube dipped under mercury. The water was kept boiling in the bath. A good deal of carbonic anhydride escaped. When most of the carbonate had been volatilized a small quantity of liquid only remained in the retort. The distillation was then arrested. The liquid in the retort proved to be a weak solution of normal carbonate (p. 205). The product of the distillation was sensibly moist when collected. A sample from the thickest part of it was analysed.

1·2592 grms. yielded ·6531 grm. of carbonic anhydride and 1·2196 grms. of ammonium chloride, = ·3879 grm. of ammonia.

These numbers indicate a composition the same as that of the carbonate at present in commerce with 7 per cent. additional water—

	Calc.	Expt.
Carbonic anhydride	52·13	51·87
Ammonia	30·21	30·80
Water	10·66	—
Additional water	7·00	—
	100·00	

Distillation of the Half-Acid Carbonate.—This was performed by Rose. He obtained a product having the composition of the commercial carbonate with 10 per cent. additional water (p. 238).

It appears therefore that when the normal carbonate is distilled slowly enough, the products are carbamate and water, and that when the acid carbonate is similarly distilled, the product is the acid carbonate again; but that when either the normal, the acid, or the half-acid carbonate is distilled faster than the whole of the products of distillation can condense in the receiver, partial condensation takes place in such a way that the carbonate of commerce is formed, according to the respective equations:

$$2[CO_2+2OH_2+2NH_3]=(CO_2)_2OH_2(NH_3)_3+3OH_2+NH_3$$
$$3[CO_2+OH_2+NH_3]=(CO_2)_2OH_2(NH_3)_3+2OH_2+CO_2$$
$$3[3CO_2+4OH_2+4NH_3]=4[(CO_2)_2OH_2(NH_3)_3]+8OH_2+CO_2$$

In these equations the whole of the water is set down, although, as part of it at first remains behind in the retort, the

reaction does not take place between the whole of it and the gaseous substances. This has been done because it cannot be said how much of the water is present during the reaction.

Products of the Slow Distillation of the Commercial Carbonate of Ammonia.

This was undertaken primarily with the motive of preparing the half-acid ammonium carbonate. It was by such a distillation that this carbonate was first obtained by Rose. He distilled the commercial carbonate at a gentle heat in a retort with its neck prolonged by a tube, the extremity of which dipped under mercury. He carried on the distillation till what remained in the retort had become perfectly fluid. This fluid on being set aside, he found deposited crystals of the half-acid carbonate, and then proved to be a solution of normal carbonate. At the time this seemed to me so remarkable a fact as to need confirmation, though since then I have, as already described, obtained a similar and even more remarkable result by acting on water with commercial carbonate until the half-acid carbonate is deposited. Rose found that the more remote part of the condensed products was neutral in composition, a fact which had already been pointed out by Dalton and John Davy. The bulk of the product he found to have a composition nearly that of the carbonate at present in commerce, though he attributed a different and more complex composition to it. In my experiment I also obtained a neutral product, but one much less hydrated than Rose's product (pp. 175, 255). The bulk also of the product proved to be almost identical with the commercial carbonate; but I obtained scarcely any fluid in the retort.

The following are the details of the distillation I performed. The apparatus was arranged as I have already described, and in accordance with Rose's description. The retort was heated by a water-bath. The temperature of the bath was from 55° to 75°; the quantity of commercial carbonate used was about 250 grammes; the duration of the distillation was about 90 hours. At the very beginning of the operation, as in all the other distillations, a little fluid formed, changing into needles.

No carbonic anhydride, that is, practically none, escaped; in Rose's experiment this gas escaped at first; but then he worked with the carbonate formerly in commerce. The deposit

was moist when first formed, but gradually became dry. It was translucent and crystalline, and its inner surface was warty and crystalline. The outer surface of it was soft and friable. The existence of two principal layers was evident in many parts of the deposit, the outer layer being less translucent than the inner. The part of the deposit nearest the body of the retort was very thin and more or less opaque as if from change. The most remote part was also very thin and looked like decomposed acicular crystals. The deposit was removed by breaking up the retort and bottled as quickly as possible.

·8716 grm. of the most remote and very thin part of the deposit, scraped off the glass in powder and therefore probably a little altered in composition, gave ·4389 grm. of carbonic anhydride, and ·7530 grm. of ammonium chloride, = ·2395 grm. of ammonia.

These numbers indicate a composition equivalent to that of the commercial carbonate, with a little loss of ammonia, and 12 per cent. additional water, as the following calculation shows:—

	Calc.	Expt.
Carbonic anhydride	49·33	50·36
Ammonia	28·58	27·48
Water	10·09	—
Additional water	12·00	—
	100·00	

·7733 grm. of the part next to the last, and intermediate in structure and position to this and the translucent mass of the deposit, thin, and probably a little changed by exposure, gave ·4095 grm. of carbonic anhydride, and ·7210 grm. of ammonium chloride, = ·2293 grm. of ammonia.

These numbers indicate a composition equivalent to that of the commercial carbonate with slight loss of ammonia, and about 6½ per cent. of additional water, as appears by the following table:—

	Calc.	Expt.
Carbonic anhydride	52·41	52·96
Ammonia	30·37	29·65
Water	10·72	—
Additional water	6·50	—
	100·00	

The remote part of the thick translucent deposit was examined. It consisted generally of a thicker, less translucent, outer layer, and a thinner, translucent inner layer.

Details of two analyses of the outer layer have been already given among the analyses of the ammonium carbamate obtained in different ways (*h*, p. 222-3). This part of the sublimate was nearly neutral, and contained only a little water. The calculated numbers indicate more exactly the formulæ

$$(CO_2)_4(OH_2)_{1\frac{2}{3}}(NH_3)_7 \text{ and } (CO_2)_4(OH_2)_{1\frac{2}{3}}(NH_3)_7,$$

as is shown in the following table:—

	Calc.	Expt.	Calc.	Expt.
Carbonic anhydride .	54·97	54·87	54·15	54·52
Ammonia	37·16	37·27	36·62	36·19
Water ($1\frac{2}{3}$ at)	7·87	—	($1\frac{2}{3}$ at) 9·23	—
	100·00		100·00	

1·1087 grms. of the inner layer of the same part of the deposit as the last, gave 1·2032 grms. of ammonium chloride, = ·3827 grm. of ammonia.

The carbonic anhydride not being determined in this case, the composition of this layer cannot be accurately formulated. The carbonic anhydride may be assumed pretty safely to have been about 54·5 per cent., which, with the calculated number for the ammonia, = 34·51 per cent., indicates about the composition represented by the formula $(CO_2)_3(OH_2)_{1\frac{2}{3}}(NH_3)_5$.

The part of the thick translucent deposit, about central, and having the two layers well marked in it, was next analysed. The thickness of the outer to the inner layer was about 2 : 3.

·9479 grm. of the outer layer (with the outer surface scraped off), gave ·5168 grm. of carbonic anhydride, and 1·0142 grms. of ammonium chloride, = ·3226 grm. of ammonia.

These numbers indicate a composition equivalent to that of the commercial carbonate, with about 2·5 per cent. additional ammonia, or a ratio of about $3\frac{2}{9}$ atoms of ammonia to 2 of carbonic anhydride.

	Calc.		Expt.
Carbonic anhydride	54·65		54·52
Ammonia	31·67	34·17	34·03
Additional ammonia	2·50		
Water	11·18		—
	100·00		

1·2017 grms. of the soft outside surface of the part last analysed, more or less changed by exposure, no doubt, gave ·6603 grm. of carbonic anhydride, and 1·3525 grms. of ammonium chloride, = ·4302 grm. of ammonia.

These numbers indicate a composition corresponding to the formula

$$(CO_2)_3(OH_2)_{14}(NH_3)_5,$$

as the following comparison shows:—

	Calc.	Expt.
Carbonic anhydride	55·11	54·95
Ammonia.....	35·49	35·80
Water	9·40	—
	100·00	

1·0393 grms. of the inner and more translucent layer of the same part gave ·5654 grm. of carbonic anhydride, and 1·0482 grms. of ammonium chloride, = ·3334 grm. of ammonia.

These numbers indicate a composition equivalent to that of the commercial carbonate, with a very slight excess of ammonia, and 2·5 per cent. of additional water:—

	Calc.	Expt.
Carbonic anhydride	54·65	54·40
Ammonia.....	31·67	32·08
Water	11·18	—
Additional water.....	2·50	—
	100·00	

1·1660 grms. of the nearer part of the thick translucent deposit (not in well marked layers) scraped free from outer and inner surfaces, gave ·6387 grm. of carbonic anhydride, and 1·1957 grms. of ammonium chloride, = ·3803 grm. of ammonia.

These numbers approach more nearly than the last those indicating the composition of the theoretically pure commercial carbonate. They show about 1 per cent. excess of ammonia and water together, and are practically identical with those of the carbonate as it occurs in commerce:—

	Calc.	Expt.
Carbonic anhydride	56·05	54·78
Ammonia.....	32·48	32·61
Water	11·47	—
	100·00	

·9534 grm of the warty inner surface-layer of the same part gave ·4923 grm. of carbonic anhydride, and ·8543 grm. of ammonium chloride, = ·2688 grm. of ammonia.

These numbers indicate a composition equivalent to that of the commercial carbonate, with a little loss of ammonia, and $9\frac{1}{2}$ per cent. additional water :—

	Calc.	Expt.
Carbonic anhydride	50·72	51·64
Ammonia.....	29·40	28·19
Water	10·38	—
Additional water	9·50	—
	100·00	

·6849 grm. of the nearest and thin part of the deposit gave ·3567 grm. of carbonic anhydride, and ·5820 grm. of ammonium chloride, = ·1851 grm. of ammonia.

·8159 grm. of the same gave ·4195 grm. of carbonic anhydride, and ·6561 grm. of ammonium chloride, = ·2087 grm. of ammonia.

These numbers indicate a composition expressed by the formula

$$(CO_2)_3(OH_2)_3(NH_3)_4$$

as the following comparison shows :—

	Calc.	I.	II.
Carbonic anhydride ..	51·97	52·08	51·42
Ammonia	26·77	27·03	25·58
Water.....	21·26	—	—
	100·00		

From the results of these analyses it appears that in distilling the commercial carbonate very slowly, a thin film of liquid first condenses, which soon becomes a thin layer of crystals, probably of normal carbonate. Next, after a cessation in the volatilization during which the temperature rises several degrees, some moist ammonium carbamate deposits. (This is really the first product of the distillation, the normal carbonate being only the product of the action of moisture—that adhering to the carbonate and to the retort and that in the air—on the ammonia and carbonic anhydride into which some of the carbamate of the commercial salt always passes when placed in a fresh volume of air. pp. 180–1.)

After this, slightly moist commercial carbonate [$(CO_2)_2OH_2(NH_3)_3$] is deposited, forming the great bulk of the products. Lastly, a very thin layer of moist and more acid carbonate is formed either by direct condensation or else by the action of water and carbonic anhydride on the superficial part of the commercial carbonate already deposited. The small quantities obtained of $\frac{4}{7}$, $\frac{3}{5}$, and $\frac{3}{4}$ carbonates were probably only mixtures of commercial carbonate with the slightly hydrated carbamate and with acid carbonate respectively. Even, therefore, when the commercial carbonate is distilled very slowly indeed, the product consists principally of the same substance; by a more rapid distillation the product would, no doubt, consist almost entirely of it. For, firstly, the refined carbonate of commerce has the same composition as that of the commoner kind; secondly, Rose's distillation of the carbonate then in commerce yielded him the carbonate now in commerce (p. 237); and thirdly, the product of the distillation—not too slow—of either the acid, half-acid or normal carbonate has the composition of the commercial carbonate (p. 265). The quantity of free and combined water in the deposit increases from the outer to the inner layer: this is explained by the fact that it corresponds with the increase of the heat applied to the retort and, therefore, to the increase in the rate of the evaporation of the water.

Products of the Distillation of the Carbonate formerly in Commerce.—These have been examined by Rose. I have not succeeded in getting a carbonate of the composition the commercial substance used to have. But I have already shown that the main product obtained by Rose had the composition of the carbonate at present in commerce plus water (pp. 237–8). Unlike, therefore, the present carbonate, it yielded a product essentially different from itself by slow distillation. The remote part of the deposit was neutral (p. 266).

Commercial Carbonate distilled with enough Water to cover it.—The effects of this distillation carried on at as low a heat as possible have been already described, so far as the changes in the retort are concerned (p. 244). The deposit was formed by a distilling heat of about 53° in a very warm condenser. It was moist and crystalline, and appeared qualitatively to be slightly ammoniacal acid-carbonate. Analysis proved it to be so.

1·4925 grms. neutralized a volume of standard sulphuric acid equivalent to ·3281 grm. of ammonia, = 21·98 per cent.

Commercial Carbonate distilled with Spirit of 90 *per cent.*— Hünefeld* ascertained that by distilling the commercial carbonate with spirit, a deposit condensed which was neutral in composition. I have repeated his experiment and have partly described the results (p. 248). The deposit was crystalline and saturated with spirit. The distilling temperature was about 60°; the condenser was warm.

·7510 grm. of the deposit in the wet state neutralized acid equivalent to ·2610 grm. of ammonia, = 34·75 per cent.

It was ascertained to be exactly neutral in composition by careful testing with calcium chloride solution. A portion of it was set fire to: when most of the spirit had burnt off, the deposit was still very moist. In its appearance and crystalline structure, it seemed scarcely, if at all, changed. The outside was scraped off, and the scraped wet lump analysed and found to contain 38·45 per cent. of ammonia. Details of this analysis have been given in the section on the carbamate (*k*, pp. 222–3).

From these results I consider that, when the commercial carbonate is distilled with strong spirit, ammonium carbamate condenses impregnated with aqueous alcohol.

Products of the Distillation of the Ammonio-Magnesian Carbonate.

This carbonate heated in a retort was found to require a temperature approaching the boiling point of water to distil anything from it. At first only a fluid distillate formed. This gradually crystallized, and much of it became solid.

The formation of a liquid distillate became less and less, and then an ordinary solid incrustation formed in the nearer part of the neck of the retort. The distillation was not carried to a conclusion. The residue in the retort was dry. It was not analysed. The fluid distillate was examined and found to contain more than two atoms of ammonia to one of carbonic anhydride. Thus, after precipitation with calcium chloride, and standing with excess of it for some days, it did not precipitate on boiling, smelt of ammonia, was alkaline to test-paper, and with carbonic acid-water in presence of the calcium chloride,

* Journal für praktische Chemie, vol. vii, p. 25.

gave a relatively copious precipitate on standing. The crystals deposited by the distillate appeared like the half-acid carbonate and proved to be this salt. The remoter part of the solid deposit in the neck of the retort proved also to be the half-acid carbonate. Its analysis, with that of the crystals from the distillate, has already been given in the section on the half-acid carbonate (IV and V, p. 193).

·8850 grm. of the deposit nearest the body of the retort, translucent, gave ·4469 grm. of carbonic anhydride and ·6607 grm. of ammonium chloride, = ·2101 grm. of ammonia, corresponding to 50·50 per cent. and 23·74 per cent. respectively; so that the solid product of the distillation is essentially the half-acid carbonate, the deposit nearest the heat being this carbonate mixed with the acid carbonate.

The Single or Chemical Substances that are produced by Condensing Mixtures of Carbonic Anhydride, Ammonia and Water.

We may now consider what are the single substances that are produced by the condensation of the mixtures of gases obtained in the various distillations which have been described, and the conditions necessary for their productions.

From the destructive effects of heat on the ammonium carbonates, the variation in the nature of the products of the distillation cannot be attributed to the effects of the heat at different temperatures on these salts. The only effect that variation in the degree of heat employed can produce is to send a variable quantity of water into the mixture of gases undergoing condensation. The modification produced in the products obtained by slow and rapid distillation is due apparently to the temperature of the condensing-tube, to the quantity of water, and particularly to the rate at which the gases are sent along the tube.*

Ammonium Carbamate.—In the dry state carbonic anhydride and ammonia combine to form carbamate, in whatever proportion they may be mixed together, the excess, if there be any, of either gas remaining free.

In the moist state these gases can still combine so as to form

* Quel que soit le sel sur lequel on agit, le premier effet de la chaleur est la dissociation des éléments; leur recomposition s'effectue ensuite d'une manière variable, suivant la température du récipient, la quantité d'eau en liberté, etc.—H. St. Claire Deville, Ann. de Chimie [3], vol. xl, p. 87.

carbamate, provided the ammonia has to the carbonic anhydride the proportion of at least two atoms to one. This is abundantly proved by the experiments recorded in this paper. Not to take special account of the fact (p. 215, *d*) that carbonic anhydride passed into ammonia-water forms carbamate instead of carbonate, there are the others (1) that on distilling sal-ammoniac with chalk or with a fixed alkaline carbonate, by which, in each case, equivalent quantities of the two gases are liberated along with water, the solid products prove on analysis to be carbamate, mixed with a little normal carbonate and uncombined water (pp. 255, 259), and (2) that on distilling a partially hydrated carbamate (Rose), or the normal carbonate, carbamate, with only a little carbonate, is formed (p. 262).

The conditions for the formation of the carbamate are, therefore, either the absence of water, or else the presence of ammonia in the proportion of at least two atoms to one of carbonic anhydride, and a little water in the liquid state.

Acid Ammonium Carbonate.—This substance can be obtained almost pure by the condensation of its constituents (p. 199), and as when thus obtained it is usually beautifully crystalline and translucent, there can hardly be any hesitation in concluding that it is a direct product of the condensation, and not a result of the union of carbamate or commercial carbonate with carbonic anhydride and water.

The condition for its formation seems to be the introduction of equal volumes of water-vapour and ammonia into carbonic anhydride, so slowly that the water is never in sufficient quantity to pass its point of maximum density at the temperature of the condenser, and therefore to condense to the liquid state. For if the water-vapour is deficient in quantity, dry compounds or mixtures containing carbamate must form; while if the water is sent into the condenser too fast—even though not so as to get in excess of the ammonia—wet compounds (or mixtures) containing carbamate appear always to be formed.

Commercial Carbonate.—An oft adduced argument in favour of this being a single substance is that based on its crystalline structure; but this loses much of its weight from the fact that both the carbamate and the acid carbonate have, as products of condensation, an apparently similar crystalline structure. Against its being a single substance has been adduced the fact that the products of the condensation of the gases in question may vary

greatly in composition. But this argument, I consider, loses all its weight through the fact that all these products when dry have a composition equivalent to mixtures of either carbamate or acid carbonate with the commercial carbonate. The grounds on which I regard it to be a single substance are, firstly, that it is formed so unfailingly and readily by the distillation—not too slow—of any of the true ammonium carbonates, or of a less hydrated compound than these when water is mixed with it before distilling; secondly, that it can be distilled and its products again readily condensed to a substance of the same composition; thirdly, that its composition when prepared under varying conditions is closely in accordance with the calculated numbers (having only, but always, a very slight excess of ammonia and a little water); fourthly, that its composition is relatively a very simple one; fifthly, that ammonium carbamate combines apparently with acid potassium carbonate (p. 250); and, sixthly, that no other products can be prepared by distillation, of uniform composition, but the commercial carbonate, the carbamate and the acid carbonate, and be re-distilled and condensed into products of the same composition again. The extent to which circumstances may vary during the formation of the commercial carbonate is shown by the different structural appearance it may have without practically varying in composition, and by the fact that, on the one hand, the quick distillation of the acid carbonate yields the commercial carbonate and free carbonic anhydride, while, on the other, the distillation of normal carbonate yields the commercial carbonate and free ammonia.

The deviation in composition from the calculated numbers (p. 237) can only, from its slightness, be attributed to a secondary reaction, in which the pure substance unites with a little of the water which always condenses with it, and with a little ammonia dissolved in this water. Were the ammonia and the water to be found sometimes in deficit as well as sometimes in excess, this fact would form an argument against the commercial carbonate being a single substance. But as the fact really stands, it signifies nothing more than does that of the normal carbonate being found, on analysis, to have lost a little ammonia by the exposure it has had to undergo.

The conditions which seem to be necessary to the sure formation of the commercial carbonate are, (1) the cooling of a mixture of two vols. of carbonic anhydride and three

vols. of ammonia in presence of at least the calculated quantity of water; or (2), the cooling of a mixture of more than two vols. of carbonic anhydride to three of ammonia in presence of at least enough water, provided that some of this is in the liquid state; or (3), the cooling of a mixture of less than two vols. of carbonic anhydride to three vols. of ammonia in presence of enough water in the state of vapour at the temperature at which they combine. Such, at least, are the conditions which the facts recorded in this communication have suggested to me; but these facts require more particular study before any interpretation of them can be very confidently accepted.

An attempt may now be made to explain what takes place in the several distillations which have been described. When the *normal carbonate* is only heated just sufficiently to decompose it, the two gases escape with a little only of the liberated water, so that water collects in the retort in considerable quantity; the moist gases entirely condense to ammonium carbamate and a little carbonate (p. 261). When the normal carbonate is heated a little higher, water rising in vapour with the gases in sufficient quantity, commercial carbonate is formed, and the excess of the ammonia left free (p. 262). When *sal-ammoniac and chalk* are distilled, two vols. of ammonia, one of carbonic anhydride, and one of water-vapour are simultaneously generated, of which much of the water condenses before the temperature is low enough for the gases to combine: then in presence of the liquid water in the condenser the gases combine so as to form ammonium carbamate and a little carbonate (p. 255). When *potassium* or *sodium carbonate* is used in place of chalk, the results are the same (p. 260). In each case the extent to which the carbamate becomes hydrated, depends upon the time during which it is in contact with the liquid in the condenser. Its re-distillation with water is like a distillation of normal carbonate. When the *acid carbonate* is distilled, the gases at first escape in equal volumes and with most of the liberated water, but as the remaining acid carbonate grows moist, the proportion of the ammonia somewhat diminishes, and along with a little water, a small quantity of half-acid and then normal carbonate collects in the retort. The distillation being so carried on that the water is present with the gases in sufficient quantity to partly condense to the liquid state before combination of the gases occurs, commercial carbonate forms and

some carbonic anhydride is left free (p. 265). The distillation being so carried on that no water condenses and yet is present in the proportion of one atom to one of ammonia at the temperature at which the gases combine the solid which forms is the acid carbonate (p. 263): such a proportion of water-vapour can only exist in presence of sufficient inactive gas, such as air or excess of carbonic anhydride. When the *half-acid carbonate* is distilled, carbonic anhydride and ammonia come off at first in the proportion of three volumes to four, together with some only of the water in the salt; but as water collects in the retort the proportion of carbonic anhydride escaping must increase, and the contents of the retort become after a time a solution of normal carbonate—such being the known effects of heat on a solution of more or less acid carbonate. The gaseous products of decomposition, being like those formed in the quick distillation of the acid carbonate, form commercial carbonate—some water and carbonic anhydride being left free (p. 265). When the *ammonio-magnesian carbonate* is distilled, so much water is given off as to hold the first-formed products of the union of the gases in solution: the volume of ammonia liberated is, at first, twice that of the carbonic anhydride, but slowly becomes somewhat less: the carbamate formed at first is soon converted in solution into the normal carbonate, and the liquid in the receiver gradually becomes such a concentrated solution of slightly acid carbonate as to deposit crystals of half-acid carbonate: lastly, as the free water becomes less, and the proportion of the carbonic anhydride (derived in part from the magnesium carbonate) becomes greater, some acid carbonate forms, along with more half-acid carbonate (p. 272). When the *commercial carbonate* is slowly distilled, the ammonia escapes in greater proportion to the carbonic anhydride than three vols. to two, along with only a part of the water liberated, so that commercial carbonate first forms, and then some more or less hydrated carbamate; but the gases and water soon come off in the proportion in which they exist in the commercial carbonate, and then combine to form simply this substance again; at last, the ammonia becoming deficient, a small quantity of a more acid and hydrated product (half-acid carbonate?) is formed (pp. 270–1). When the *carbonate formerly in commerce* is slowly distilled, the ammonia in the first stage is not in as great proportion to the carbonic anhydride as it is in the first stage of

the distillation of the carbonate at present in commerce, but the water is in insufficient quantity for the conversion of the whole of the ammonia into the modern commercial carbonate, and therefore after some of this substance has deposited, some partially hydrated carbamate forms, and some carbonic anhydride remains free (the carbamate is more hydrated—pp. 175, 218—than that obtained in distilling modern commercial carbonate, because of the greater proportion of water in the old carbonate); as the distillation proceeds, water collects in the retort, and, the heat required for continuing the distillation rising, enough water evaporates to convert all the ammonia into commercial carbonate, the product that then forms (p. 271).

The Carbonate of Ammonia formerly in Commerce not a Single Substance.—This can hardly be regarded as such because, firstly, it is not very uniform in composition; secondly, it cannot apparently be distilled, so as to yield a substance of the same composition again; thirdly, its composition is complex and peculiar for a single substance, and, at the same time, allows of its being regarded as a mixture of the two much better defined products of distillation, namely, acid carbonate, and the carbonate at present in commerce, this mode of viewing it being supported by the nature of its variations in composition (p. 232).

Rose's Salt of the composition—

$$(CO_2)_2OH_2(NH_3)_4$$

and Thomson's Normal Carbonate—

$$CO_2OH_2(NH_3)_2$$

not Single Substances.—If such a substance as that obtained by Rose by distilling the carbonate formerly in commerce at a gentle heat, and by distilling a mixture of sal-ammoniac and sodium carbonate (p. 175), really exists, it is quite analogous in constitution to the commercial carbonate, being a compound of carbamate with anhydrous normal metacarbonate, instead of with acid metacarbonate, thus:—

Commercial carbonate $C(NH_2)O_2NH_4,CO_3NH_4H$
Rose's salt $C(NH_2)O_2NH_4,CO_3(NH_4)_2$.

An argument in support of its being a single substance is that there exists, according to Rose,* a compound having the formula—

$$(SO_3)_2OH_2(NH_3)_4;$$

* Pogg. Ann., vol. xlix, p. 183. Taylor's Scientific Mem., vol. ii, p. 551.

but this substance does not seem to be very well defined. Still I do not think we are justified in believing it to be a single substance, for, first, by a similar distillation of sodium or potassium carbonate or of chalk with sal-ammoniac, I have obtained, as already described (pp. 255, 260), *wet* sublimates varying in composition, as regards water—free and combined, between that indicated by the above formula and that with one atom of water to one of carbonic anhydride (on keeping these got dry by combining with the moisture, but this does not prove anything); secondly, by distilling the commercial carbonate with sufficient care, I have obtained, as already described, deposits very nearly neutral in composition with a much smaller proportion of water; thirdly, Rose did not himself obtain a product of essentially the same composition in every experiment, and found, besides, that it yielded a still less hydrated compound when distilled; fourthly, it is not a compact translucent deposit.

Evidence of the definite nature of Thomson's normal carbonate is entirely wanting, and nearly the same arguments can be brought against its existence.

Rose's $\frac{5}{8}$ *Carbonates,* $\frac{7}{8}$ *Carbonate, and his Hydrated Acid Carbonate, not Single Substances.*—Judging from my own experiments, these products of distillation must all have been obtained in the wet state at first, so that we have no evidence of their being definitely hydrated single substances. A revision of the atomic relations of the ammonia and carbonic anhydride in the $\frac{5}{8}$ carbonates has been made at pp. 237–8, and in the $\frac{7}{8}$ carbonate at p. 264.

CORRIGENDA.

Page 173, line 2 from top, for "carbonate," read "carbamate."
„ „ „ 18 „ dele "then."
„ 176, „ 16 from bottom, for "carbonate," read "carbamate."
„ 181 „ 18 „ omit the sentence beginning "Further."
„ 199, lines 12 and 13 from top, for "both these cases," read "in the latter case."
„ „ line 16 from top, insert "(p. 215)."
„ 205 „ 20 „ after "carbonate," insert "solution."
„ 214 In the remarks on the existence of a normal orthocarbonate, Dalton's statement that he obtained a solution of subtricarbonate (p. 233), ought to be adduced as additional evidence of it.
„ 238, line 10 from top, the calculation for 8½ per cent. additional water agrees still more closely with Rose's numbers.
„ 241, line 11 from bottom, for 236 read 237.

XXIV.—*Account of a Gas Furnace for Chemical Operations at a White Heat, without the aid of a Blowing Machine.*

By Charles Griffin.

Fusions at a white heat can be readily effected by a gas furnace supplied with air by a blowing machine. But a furnace of that description has several defects: the blowing machine is expensive; it is cumbersome in a laboratory; it demands constant labour during a fusion; and it produces so much noise as to interrupt every kind of quiet work.

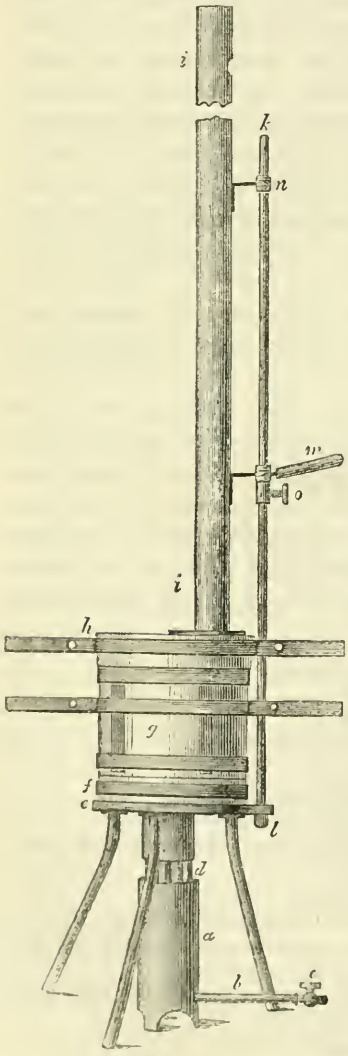


Fig. 1.

The furnace to be described in the following notes is free from these defects. It is small and portable, easily put together and taken asunder. It demands no blowing machine, and only a small chimney. It acts without smoke, or dust, or noise. Its heating power is sufficient to raise a 4½-inch clay crucible, filled with metal, to a white heat. Cast iron can be fused in it, and cast into ingots of the following weights:—

A. Commencing with the furnace cold:

An ingot of 2 lbs. in 70 minutes.
An ingot of 3 lbs. in 90 minutes.
An ingot of 4 lbs. in 2½ hours.

B. Commencing with the furnace hot:

An ingot of 2 lbs. in 40 minutes.
An ingot of 2½ lbs. in 50 minutes.
An ingot of 5 lbs. in 2½ hours.

Silver, gold, and copper can be fused in larger quantities and in less time.

The furnace is represented by Fig. 1. Its height, including the stool, is about 2 feet. The external diameter is 8 inches. It consists of the following parts:—

a is a brass cylinder, open at the bottom, and into the top of which 16 Bunsen's burners are fixed; gas is supplied by the pipe *b*, regulated by the stopcock *c*. A jacket surrounds the upper part of the Bunsen's burners, but is cut away at the bottom *d*, in order to permit air to pass up between the burners.

The consumption of gas by this compound burner when at work in the furnace is 33 cubic feet per hour.

e is an iron stool which supports the furnace and also the iron rod *k*, to which the chimney is attached.

f is a fire-clay sole plate, shown in section by Fig. 2. The system of burners is closely fixed in the perforation of this plate.



Fig. 2.

g is a cylinder of fire-clay, shown in section by Fig. 3. It measures 6 inches in height, 8 inches in external diameter, and 5 inches in bore. The crucible to be heated is supported on a perforated plumbago cylinder, represented in section by Fig. 3, and in perspective by Fig. 4. In order to secure the greatest degree of fusing power, the bottom of the crucible *c*, Fig. 3, should be fixed at 1-inch or $1\frac{1}{4}$-inch distance from the face of the bundle of gas burners *a*, Fig. 1. For this purpose the two plumbago cylinders supplied with the furnace differ $\frac{1}{2}$-inch in height.



Fig. 3.



Fig. 4.

The crucible must be conical, not barrel-shaped, in order that the flame, after striking the crucible, may have space to escape through the holes in the plumbago cylinder.

The distance between the outside of the plumbago cylinder and the inside of the furnace cylinder, that is to say, the

space marked *s*, *s*, in Fig. 3, must not exceed ½-inch all round. Increase of space here lessens the heating power of the furnace.

h, Fig. 1, is the dome or roof of the furnace. It is represented in section by Fig. 5. This figure shows that the flame in rising from the body of the furnace is bent twice at a right angle before it passes into the chimney.



Fig. 5.

i, *i*, Fig. 1, is an iron chimney, which measures 4 feet in length and 2 inches in diameter; *k* is a vertical iron rod, screwed into the stool *e* of the furnace at *l*. This chimney is movable by the handle *m*. At *n* there is a guide, and at *o* a stop. By this arrangement the chimney can be set on the furnace, or moved aside, with facility. This movement is sufficient when the furnace is used for simple fusions, or when no deleterious gases are driven off; but when arsenic, sulphur, &c., are expelled during an operation, and the entire apparatus cannot be placed under a hood or fixed chimney, then the upper end of the chimney *i*, *i*, should be passed into the vertical branch of a knee-piece, the horizontal branch of which is connected with a fixed flue, and the chimney *i*, *i*, should be raised within the knee-piece by moving upwards the stop *o*, on the rod *k*. A rise of about 6 inches is necessary to make room for the removal of the dome *h* and the cylinder *g*, on dismounting the furnace to remove a crucible. It is necessary to see that the draught of the fixed chimney is not too powerful.

The method of mounting crucibles exhibited by Fig. 3 serves for 4½-inch and for 4-inch crucibles, but not for smaller sizes. A 3-inch crucible slips through the plumbago cylinder and spoils the draught, and if a smaller cylinder is used, the spaces *s*, *s*, Fig. 3, become so wide that the effective heat of the furnace is greatly diminished. Hence it is necessary, when small crucibles are to be used, to support them on a grate made of fire-clay, the best form of which is represented by Fig. 6. Its diameter is 6 inches. This grate is placed upon the sole-plate of the furnace. The crucible is set upon it, and is surrounded by a smaller fire-clay furnace cylinder, namely, by one that measures 5 inches



Fig. 6.

in height, 6 inches in external diameter, and 4 inches in bore. The dome, Fig. 5, or *h*, Fig. 1, is used with the small cylinder, Fig. 7, as well as with the large cylinder, Fig. 3.

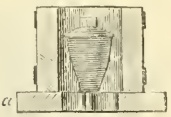


Fig. 7.

Platinum and porcelain crucibles can be heated in the small furnace, Fig. 7, enclosed in fire-clay crucible cases.

The fire-clay grate, Fig. 6, can be used with the large cylinder, Fig. 3; and, in crucibles supported by it as much as 3 lb. of cast-iron can be melted; but the operation requires an extra half-hour of ignition beyond that required when the crucible is supported by the plumbago cylinder, Fig. 4.

When the furnace is mounted for use with the large cylinder, Fig. 3, three bronze pennies are put on the sole-plate *f*, Fig. 1, to support the cylinder *g;* when the grate is used, the three pennies are put under the extreme edge of the grate. These pennies leave a space for the admission of air.

Operations which succeed at moderate temperatures, such as the fusion of zinc in an iron pot or ladle, are performed without using the dome and chimney. The vessel to be heated is to be placed on the inner cylinder of Fig. 3.

The furnace body, Fig. 3, and the dome, Fig. 5, are provided with iron handles. These never become very hot, not even when the furnace contains 3 lbs. of melted iron. The operator's hands are sufficiently protected when lifting these pieces by a couple of folds of thick cloth, or brown paper. The small cylinder, Fig. 7, is handled by the same bow tongs that serve to lift the hot crucibles.

Access to the crucible in the furnace is gained at any moment by turning aside the chimney, and lifting the dome *h*, Fig. 1. When the crucible is to be removed, the dome is first taken from the furnace, and placed on a circular plate of fire-clay; the outer cylinder is next lifted off, and placed on a similar plate of fire-clay. The crucible can then be removed by the bow tongs. If the furnace is to be immediately used for a second operation, the cylinder should be covered with a third clay plate, to retard the loss of heat while the crucible is being replaced by another.

Gas Muffle Furnace.—When the furnace cylinder *g*, Fig. 1, is replaced by an oval furnace body which contains a muffle, as represented by M in Fig. 8, all other parts of the furnace

remaining as represented by Fig. 1, the usual muffle operations can be performed, such as cupellation, the roasting of ores, the combustion of organic bodies for their ashes, the burning of filters, &c. The muffle belonging to this furnace measures 7 inches in length, $3\frac{1}{2}$ inches in width, and $2\frac{1}{2}$ inches in height. It acquires a bright red heat, sufficient to melt silver, gold, and copper. This heat can be kept steady and uniform for hours; and being free from dust or soot, is particularly suitable for such operations as annealing.

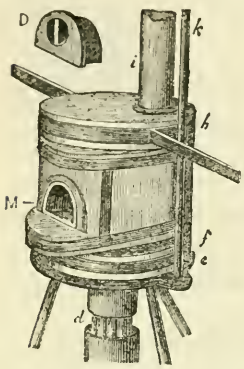


Fig. 8.

Nothing new is offered in the burner of this apparatus, for it is merely a bundle of Bunsen's jets, nor in the fire-clay fittings, which are copied from Griffin's Blast Gas Furnace; but a few words may be said on one or two other points.

The first relates to the supply of gas and air. The greatest heat is produced when coal gas is burnt in the presence of as much air as entirely decomposes and oxidises it; that is to say, when one volume of gas is mixed with ten or twelve volumes of air; but when gas is mixed directly with so large a quantity of air, it becomes explosive, and cannot be used as fuel. It is consequently necessary, in the management of a gas furnace, to supply the air, certainly as rapidly as the combustion demands, yet so gradually as to avoid explosions. In arranging the furnace now under discussion, the gas is supplied in excess, and the air in three successive doses:—the first quantity at the bottom of the cylinder *a*, Fig. 1; the second at the openings *d*, Fig. 1; and the third, where the three bronze pennies are placed on the sole-plate, either under the cylinder, Fig. 3, or the grate, Fig. 6. By this arrangement, the gas is fully supplied with air, while the chance of explosion is almost entirely obviated. When, however, the furnace is in operation at a white heat, if the gas supply-pipe is *pinched*, an explosion occurs, because, under the action of the hot furnace and the chimney, the air is immediately brought into excess. In such a case, as soon as an explosion is heard, the gas should be turned off, the chimney be moved aside, and the opening in the dome of the furnace be closed by a crucible cover. The draught of air is thus stopped.

If now the gas is turned on fully, it takes fire properly in the body of the furnace, and, the chimney being replaced, the operation proceeds as usual.

The second point to be noticed is the form of the flue in the furnace roof, or dome, Fig. 5. By this contrivance, the rising current of flame and gas is bent twice at a right angle, and an obstruction is produced between the body of the furnace and the chimney, without which the gases would escape too readily into the chimney, and burn there instead of in the furnace. If the roof, Fig. 5, is replaced by a flat perforated plate similar to Fig. 9,— the same furnace and chimney being used,— the diminution of heating power is very considerable.



Fig. 9.

The progress of an ignition is judged of chiefly by the colour of the fire, as seen through the crevices of the furnace between the pieces *f* and *g*, and *g* and *h*, in Fig. 1. The eye soon learns to distinguish the colour which indicates an *iron-melting* heat.

The proper admixture of gas and air is judged of from the colour and quantity of flame which passes up the chimney. To enable the operator to see this flame, three small holes are bored in the chimney. The flame is never seen at the upper hole, unless the supply of gas is too large; but it is always visible at both the lower holes. As there are no valves to regulate the supply of air, due attention must be paid to the supply of gas.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

SESSION 1869–70.

November 4th, 1869.

Sir B. C. Brodie, Vice-President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

Alfred Dudley Keightley, Old Hall, Milnthorpe, Westmorland: W. Fletcher Barrett, The Woodlands, Isleworth; John Morrison, Arklow Chemical Works, Arklow; Temple A. Orme, University College; W. G. Lewis, Oriel College, Oxford.

Mr. R. Gerstl was elected an Associate of the Society.

Discussion on Dr. Williamson's lecture on the "Atomic Theory."

November 18th, 1869.

Dr. Williamson, President, in the Chair.

The following gentleman was duly elected a Fellow of the Society:—

E. S. Blackwell, Montreal, Canada.

The following papers were read:—

"On the Formation of Carbonic Ether:" by Messrs. W. Dittmar, and George Cranston.

"On Namaqualite:" by Professor Church, M.A.

"Chemical Researches on New and Rare Cornish Minerals:" by Professor Church.

"On Chloranil and Bromanil," No. II.: by Dr. Stenhouse.

"On Salts of Acetylinated Ethyl:" by J. A. Wanklyn.

December 2nd, 1869.

Dr. Williamson, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

Sir Roderick Impey Murchison, Bart., F.R.S., &c., &c., Belgrave Square; Matthew H. Cochrane, 108, Peel Terrace, Glasgow; Thomas Walton, 3, Bourne Street, Hull; G. M. Hopwood, 22, Grosvenor Square, All Saints, Manchester; John Wiggin, Ipswich; Thomas Gibb, Bede Metal Company, Jarrow-on-Tyne; George Harrison, 26, Havelock Square, Sheffield; Edward Smith, Strand, Torquay.

The following papers were read:—

"Remarks on some Points in the Nomenclature of Salts:" by H. G. Madan.

"Results of the Analysis of Sea-Water, performed on board H.M.S. *Porcupine*, July, 1869, by John Hunter.

December 16th, 1869.

Dr. Williamson, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

Samuel Jefferson, Woodville Terrace, Woodhouse Lane, Leeds; Clement Higgins, King's College, London; James John Bowrey, Stepney Causeway.

January 20th, 1870.

Dr. Williamson, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

James Bell, Howell Hill, Ewell; Edwin Lapper, 11, Maiden Lane, Cheapside; George R. Hislop, Gas Works, Paisley; Henry Seward, 15, Barnsbury Park, N.; Alfred Bird, 69, Worcester Street, Birmingham.

The following papers were read:—

"On the Absorption of Mixed Vapours by Charcoal:" by Mr. John Hunter.

"On the Composition of Iron Rust:" by Dr. Crace Calvert.

February 3rd, 1870.

Dr. Williamson, President, in the Chair.

The following gentleman was duly elected a Fellow of the Society:—

Mr. Alexander Pedler, 12, Wood Vale, Lordship Lane, S.E.

The following papers were read:—

"On the Organic Matter contained in Air:" by Mr. E. T. Chapman.

"On some New Reactions of Alcohols:" by Mr. E. T. Chapman.

Mr. Perkin showed some experiments illustrating Berthelot's discovery of the formation of hydrocyanic acid by the direct combination of nitrogen and acetylene.

February 17th, 1870.

Dr. Williamson, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

Thomas Wills, Royal Institution, Albermarle Street; John Wortley Axe, Royal Veterinary College; Erneste Francis, Charing Cross Hospital; Thomas Glazebrook Rylands, Warrington; Dr. Rowland J. Atcherley, Edgerley Cottage, Theydon Bois, Essex; William Pritchard, 11, Oakley Square, N.W.: Arthur Bateman, Southville, Clapton; Philip Wright, Osmaston Manor, Derby; Arthur Prangley, Redland, Bristol; Lewis Buttle Ross, Great Driffield, Yorkshire.

Dr. Tyndall showed some of his experiments on the action of light upon vapours.

March 3rd, 1870.

Dr. Williamson, President, in the Chair.

The following gentleman was duly elected a Fellow of the Society:—

Christie P. Sandberg, Stockholm.

A Lecture on Refraction Equivalents was delivered by Dr. Gladstone.

The following paper was read:—

"On Kryptophanic Acid:" by Dr. Thudichum.

March 17th, 1870.

Dr. Williamson, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

D. Brown, 17, South Norton Place, Edinburgh; A. Muirhead, 44, Gloucester Road, Regent's Park; T. L. Patterson, Greenock; D. Penny, Misterton, near Gainsborough; S. J Smith, 29, Park Road, New Wandsworth.

The following papers were read:—

"On Artificial Alizarin:" by Mr. W. H. Perkin.

"On the Combinations of Carbonic Anhydride with Ammonia and Water:" by Dr. Divers.

Anniversary Meeting, March 30th, 1870.

Dr. Williamson, President, in the Chair.

The following report was read by the President:—

On behalf of the Council I feel very great pleasure in congratulating you on the rapidly increasing usefulness and prosperity of our Society.

The most interesting incident in the history of the past year has been the delivery by M. Dumas of the inaugural Faraday lecture. It was indeed an impressive tribute to the memory of our great countryman, which was paid by that noble veteran of science, and one of which the record ought to occupy a place of honour in our Journal. We still hope to receive from M. Dumas a manuscript of his classical discourse.

The Council have had the pleasure of accepting the offer of a munificent donation of palladium from Messrs. Johnson and Matthey, to be used for the preparation of the first ten Faraday medals.

Your Council have felt it to be of considerable importance to give greater publicity to the proceedings of the Society, and they have accordingly made provisional arrangements for the preparation of abstracts of the papers, and in some cases of the discussions, for transmission to such papers as desire to publish them. These abstracts already appear in several papers, and are read with interest.

Another matter of considerable importance has been brought under the notice of your Council, and has been by them referred to the careful consideration of a sub-committee, who will report to the new Council.

The great activity of chemists in France and Germany leads to the publication of vast quantities of important matter in languages not easily intelligible to many of our members; and a feeling has been entertained for some time past that the progress of our science, and of its applications, would be greatly promoted by the regular publication in the English language of accurate reports of all chemical papers. For many years past annual reports of the kind have been published in Germany, first under the auspices of the great Berzelius, and latterly under those of Liebig and Kopp. The French Chemical Society have also added very greatly to the value of their

journal, by publishing in it reports of a great number of important papers from various sources. I am happy to say that the eminent chemists who are at the head of that Society concur with us in desiring to publish reports combining the completeness of the Jahresbericht with a much greater celerity of appearance, and that our respective members may have presented to them every month an outline of all that has been done in the science since the last report. It appears that considerable facilities would be afforded for the preparation of such reports by a joint action of the two Societies, and our friends at Paris have expressed the utmost readiness to co-operate with us in this important matter. I hope at our next anniversary meeting to be able to congratulate the Society on the commencement of a system of international working.

At the time of the last anniversary meeting the number of Fellows of the Society was 522; the present number is 551, as will be seen from the following statement:—

Number of Fellows, Anniversary March 30th, 1869		522
Since elected and paid admission fees		41
		563
Removed on account of arrears	5	
Withdrawn (A. W. Gillman)	1	
Deceased	6	
	—	12
Number of Fellows, March 30th, 1870		551
Number of Foreign Members, Anniversary, March 30th, 1869		38
Deceased		2
Present number of Foreign Members		36
Associates		3

The names of the Fellows deceased are:—

E. W. Brayley, F.R.S., Julien Courtauld, Thomas Graham, F.R.S., A. B. Northcote, Dr. F. Penny, J. Wheeler.

The Foreign Members deceased are:—

Dr. Otto Linné Erdmann, and Dr. Joseph Redtenbacher.

Edward Wedlake Brayley was born September 28th, 1801; his life presents the uncommon spectacle of the attainment of a well recognized scientific position, by one who had neither the advantage of an early scientific education, nor the opportunity to render himself known by discovery. His father was a literary man of small pecuniary means, but was possessed of a good collection of books. From his mother, and from his father's books, Brayley derived all his early education; subsequently he attended the lectures of Tatum, the same to whom Faraday owed his first ideas of natural science. At a later date he became a pupil of Brande, of whom he always spoke with great respect, saying that he was one of the best teachers and lecturers he had ever known. He supported himself during the early part of his life by lecturing and teaching, his leisure only being devoted to reading and study, for the most part in the library of the London Institution. In 1836, in conjunction with Mr. Thomson, he was appointed librarian to the London Institution, and on the death of that gentleman became principal librarian, which post he held at the time of his death.

He was one of the original members of the Chemical Society, and in 1854 was elected a Fellow of the Royal Society. He was also a Fellow of most of the other learned societies of London. The death of his wife preceded his own by about a year. He died somewhat suddenly from gout in the stomach, February 1st, 1870, in his 69th year, and leaves no issue.

He was best known to scientific men as an acute commentator on the works of others. His extraordinary industry and power of memory enabled him to bring together all the known facts of a particular subject from every available source, no matter how obscure. He was always listened to with attention and respect, when he spoke at the meetings of the various learned societies of which he was a member. Both as a speaker and as a lecturer his manner was very good, and indeed his powers in the last particular were remarkable; they were the result of long practice and careful self-training.

Mr. Brayley did not contribute any paper to the Journal of the Society. His scientific works almost all related to astronomy and meteorology. Perhaps the most important of his specula-

tions related to the physical constitution of the sun, on which subject he had formed a very distinct theory; he was engaged at the time of his death on work relating to this subject.

By the death of Mr. Brayley, not only have we lost one of our most learned fellows, but also one who was always ready to afford every assistance in his power to any one engaged in scientific pursuit. In manner he was somewhat precise, though cheerful and pleasant, and was one of the most obliging and courteous of men.

His character, together with his great attainments, secured for him his well recognized reputation and general esteem.

Thomas Graham was born at Glasgow, on the 21st December, 1805, and died on the 16th of September, 1869. He was the eldest of a family of seven, of whom only one survives.

He went to the English preparatory school at Glasgow, in 1811, and was there under the care of Dr. Angus. In the year 1814 he was removed to the High School, where for four years his studies (which included the Latin language) were directed by Dr. Dymock, and subsequently for one year by the Rector, Dr. Chrystal, under whom he studied Greek. It is said that during these five years he was not once absent at school-time. In 1819 he commenced attendance in the University classes in Glasgow. Thomas Thomson then occupied the Chair of Chemistry, and young Graham benefitted by his instruction, as also by that of Dr. Meikleham, the Professor of Natural Philosophy.

By this time he had already acquired a strong taste for experimental science, and formed a wish to devote himself to chemistry. His father, an able and successful manufacturer, had formed different views for his future career, and wished him to become a minister of the Scotch Church. It is hardly to be wondered at that the father should not have seen in the prosecution of science much scope for an honourable or advantageous career; but young Graham had already seen something of the means afforded by experimental science of getting knowledge from the fountain head—from Nature herself. He felt the need of more such knowledge to mankind, and his scheme of life was formed accordingly.

After taking the degree of M.A. at Glasgow, he continued his studies for two years at Edinburgh, and there studied under

Dr. Hope, and enjoyed the friendship of Professor Leslie. On his return to Glasgow, he taught mathematics for some time at the suggestion and under the patronage of Dr. Meikleham, and subsequently opened a laboratory in Portland Street, Glasgow, where he taught chemistry. It is probable that some of the severest trials of his life occurred at about this period.

While absent from Glasgow he was in the habit of writing regularly and at great length to his mother, and from the tenor of these letters it is easy to see what that mother must have been to him. A writer on the social position of women has described the feelings of boys towards their mothers as scarcely amounting to respect! Young Graham's mother seems to have been his guardian angel, sympathising with his hopes and his sorrows; and certainly his feelings towards her would have been very inadequately described by that frigid word. While studying at Edinburgh he earned, for the first time in his life, some money by literary work, and the whole sum (£6) was expended in presents to his mother and sisters.

In 1829 he was appointed lecturer on Chemistry at the Mechanics' Institution, Glasgow, in place of Dr. Clark; but the decisive step of his life was in the subsequent year. It was in 1830 that he was appointed Professor of Chemistry at the Andersonian University, Glasgow; and it is said that his mother, who was on her deathbed, lived to hear the glad tidings of his appointment. He was now more favourably circumstanced for experimental labours, and we find that the seven years spent at the Andersonian University were years of great activity. In the beginning of the year 1837, died Edward Turner, Professor of Chemistry in the newly-founded London University, now called University College, London. Thomas Graham was the successful candidate for the vacant chair, and in August of the same year, we find him already settled in the great metropolis. It was only now that the young philosopher found adequate scope for his abilities. Young men thirsting for knowledge crowded to his lectures, and in those lectures he explained the principles of Chemical Science with an exactness and clearness never before attained. The success of these lectures was not due to eloquence, nor to any smoothness of diction, for all such matters Graham usually neglected to a degree which in an ordinary person would hardly have been

excused. He had a truly philosophical method, which carried away the listener with irresistible force, the same exactness of thought, the same logical arrangement of matter, in a word, the same purely scientific mind which pervades his work, "The Elements of Chemistry." That work, which immediately made its author's name known in all parts of the world, is too well known to the Fellows of the Chemical Society for it to be necessary to speak here of its great merits. I will merely allude to the successive editions which have appeared in England, the numerous reprints scattered about America, and the translations published in many languages. In Germany the excellent edition of Dr. Jul. Otto is still the most extensively used and the most valued book of Chemical instruction.

His investigations of the phosphates is remarkable in many ways. It was known that solutions of phosphoric acid in water vary in their properties; and chemists were satisfied with giving a name to the changes without investigating their nature. These solutions contained phosphoric acid and water, and were assumed to have like composition. They were accordingly called isomeric. Graham observed that they differ from one another in the proportion of water combined with the acid, and constitute in reality different compounds.

He knew that water combines with acids as other bases do, and he showed that the various compounds of phosphoric acid and water constitute distinct salts, each of which admits of its hydrogen being replaced by other metals without disturbance of what we should now call the type. Thus, to use our present notation, the three hydrates PO_4H_3, $P_2O_7H_4$, PO_3H, correspond to the following proportions of acid and water:—

$$P_2O_5 + 3H_2O = 2PO_4H_3$$
$$P_2O_5 + 2H_2O = P_2O_7H_4$$
$$P_2O_5 + H_2O = 2PO_3H.$$

Graham observed that the hydrate PO_4H_3 is constituted like a salt, inasmuch as its hydrogen can be replaced atom for atom by other metals, like sodium, potassium, &c., forming such compounds as PO_4NaH_2, PO_4Na_2H, &c.

In order to appreciate duly the powers of mind of the author of this admirable research, we ought to compare his methods of reasoning with those generally prevalent among contemporary

chemists, and on the other hand with the methods of to-day. One would fancy that Graham had been acquainted with the modern doctrines of types and of polybasic acids, so clearly does he describe the chemical changes in matter-of-fact language, and so consistently does he classify the compounds by their analogies. At that early period we find Graham considering hydrogen, in various salts, as a basylous metal; an idea which (in spite of its undeniable truth) some chemists of the present day have not fully realised.

Amongst minor chemical researches may be mentioned a series of experiments on the slow oxidation of phosphorus by atmospheric air. He discovered that this process (and the faint light which accompanies it) is arrested by the presence in the air of a trace of olefiant gas, $\frac{1}{450}$ of the volume of the air being sufficient for the purpose. Still smaller proportions of some other vapours were found capable of producing this same effect; spirits of turpentine being particularly remarkable, as less than a quarter of a thousandth of its vapour mixed with air was found sufficient to prevent the slow oxidation of phosphorus.

On another occasion Graham investigated phosphuretted hydrogen, and made some remarkable observations concerning the conditions of the formation of the spontaneously inflammable gas. One of these deserves especial notice; in connection with the action of olefiant gas in preventing the oxidation of phosphorus, he found that phosphuretted hydrogen is rendered spontaneously inflammable by the admixture of a very small proportion of an oxide of nitrogen, probably nitrous acid.

One of the most obscure classes of combinations are those which water forms with various salts. These bodies are characterised by the chief peculiarities which belong to definite chemical compounds; but chemists are as yet unable to explain them. Water so combined is called water of crystallisation, and is said to be physically, not chemically, combined: a very convenient way of getting rid of a difficulty, by passing it on to our neighbours.

Graham examined the proportion of such water of crystallisation in a considerable number of salts, and he moreover examined the properties which it has when so combined. He found that some of the water in an important class of sulphates is held far more firmly than the remainder, and with force equal to that with which water is held in various chemical compounds.

He showed that such firmly combined water can be replaced by salts in a definite chemical proportion. In fact, he got fairly hold of the subject by chemical methods, and laid the foundation for an explanation of it.

He discovered and examined compounds of alcohol with salts, and derived from them valuable evidence of the analogy between alcohol and water.

On a later occasion he made a series of important experiments upon the transformation of alcohol into ether and water, by the action of hydric sulphate. Liebig had endeavoured to explain the formation of ether in this process, by representing it as due to the decomposition at a high temperature of a compound of ether previously formed at a lower temperature, such decomposition being due to the increased tension of the vapour of ether at the higher temperature. Graham justly argued that if the decomposition were due to the tension of ether vapour, it would not take place, and ether would not be formed, if the tension were not allowed to exert itself. He heated the materials in a closed tube, and proved that ether was formed, although the tension of its vapour was counteracted by the pressure thus obtained.

The line of research which occupied most of his attention, and in which his results were perhaps the most important, was that of diffusion; and it would be difficult to over-estimate the importance to molecular chemistry of his measurements, of the relative velocities of these spontaneous motions of particles of matter, whether in the state of gas or in the liquid state.

It was known that 1 part by weight of hydrogen occupies the same volume as 16 parts by weight of oxygen when measured at like temperature, and under like pressure. Chemical investigations prove that these equal volumes of the two gases contain the same number of atoms. We also know that the atoms in such a gas are in rapid motion, and resist the pressure to which the gas is at any particular time exposed, by striking against the surface which presses them together with force equal to that which presses them together. Thus a given volume of hydrogen is maintained against the atmospheric pressure by an energy of atomic motion, equal to that of the same volume of oxygen. Each atom of hydrogen accordingly exerts a mechanical energy equal to that of each atom of oxygen; but we

have seen that the hydrogen atom is much lighter than the oxygen atom, and accordingly it must move with much greater velocity than the oxygen atom.

Now Graham allowed hydrogen to escape through a very small hole in a plate of platinum; and allowed oxygen to escape under similar circumstances. He found that each hydrogen atom moves out four times as fast as each oxygen atom. His experiments were so arranged as to enable him to measure the relative velocities of certain motions of the atoms —motions not imparted to them by any peculiar or unnatural conditions, but belonging to them of necessity in their natural state. He found, moreover, that heat increases the velocity of these atomic motions, whilst increasing the force with which a given weight of the gas resists the atmospheric pressure.

The phenomena of the diffusion of gases and liquids do not astonish us by their brilliancy and variety. But the immense importance of this region of experimental science dawns upon us when we remember that there is no so-called vital process which cannot ultimately be referred to a chemical process; that more or less intense chemical action takes place at all points of the frame of animals and plants; and that an essential condition of this action, and of life itself, is the carrying to and fro of materials, not only by muscular and ciliary action, but in a more intimate manner by diffusion.

The study of the condensation of gases by solids, and the combination of soluble compounds with membranes, led him to discoveries which are likely to be of great value to physiologists in explaining processes of absorption and secretion. Thus he found that oxygen is absorbed to a greater extent than nitrogen by caoutchouc, and that when a bag made of a thin membrane of this substance is exhausted by means of a good air-pump, the oxygen and nitrogen diffuse through it (probably as condensed liquids), and evaporate inside the bag in different proportions from those in which they are present in air, the oxygen rising to over 40 per cent. of the diffused air. Again, a mixture of hydrogen and oxygen was separated almost completely by the action of palladium, which condensed the hydrogen in very large quantity, and the oxygen very slightly.

Perhaps the most remarkable substances discovered in the course of his experiments on diffusion, were the soluble modifications of tungstic and molybdic acids, ferric oxide, &c.; and the

process by which these bodies were obtained was, perhaps, the most instructive part of the result, proving, as it does, that in their salts, these bodies have properties different from those which they normally possess in the free state; and retain them when the other constituent is removed by a sufficiently gentle process.

Another remarkable fact which bears on a most important theory, is the separation effected by Graham of potassic hydrate and hydric sulphate, by diffusion of potassic sulphate in aqueous solution—a fact which requires us to admit that the solution of the salt in water contains those products mixed with one another; just as much as the experiment of diffusing air through a porous clay pipe, and getting its constituents in a different proportion from that of the original air, proved that air is a mixture and not a compound of the two gases.

In many of his ideas Graham was in advance of his contemporaries, and it might be difficult to find a chemist who has dealt more cautiously with general questions and delicate experimental operations,—or one whose results, in each direction in which he has worked, may more safely be expected to stand the test of future investigations.

Augustus Beauchamp Northcote, M.A., and a Fellow of the Chemical Society since 1856, was born in London, May 1st, 1831. Shortly afterwards he went to Plymouth, where he resided for some years. His family was of Devonshire origin, and a branch of that which Sir Stafford Northcote represents. In the year 1851 he came to London, and entered at the Royal College of Chemistry. He studied there with great zeal and success, and was soon rewarded by the Professor (Dr. Hofmann) with a free scholarship. Shortly afterwards he became one of Dr. Hofmann's private assistants, and conducted in that capacity several inquiries, including the well-known investigation of the Harrogate waters. Ultimately, in the year 1855, he was appointed senior assistant in the College. Early in 1858 he went to Oxford as Demonstrator of Chemistry to Professor Brodie. In the autumn of that year he published, in conjunction with his friend Mr. A. H. Church, a Manual of Qualitative Chemical Analysis.* This book was

* Published by Van Voorst, pp. xvi, 428.

the first published in England in which the unitary notation of Gerhardt was systematically adopted. Mr. Church states that the greater part of the labour involved in the collection, arrangement, and verification of the materials of this manual was performed by Mr. Northcote. He matriculated at Queen's College, Oxford, in 1859, and was shortly afterwards appointed Lecturer on Natural Science at Exeter College. He was placed in the first class in the Natural Science School in Michaelmas Term, 1861, and graduated B.A. In 1864 he was elected Radcliffe Travelling Fellow; but in the winter of that year his health broke down, and he was obliged to resign his college lectureship. For three years he resided chiefly on the south coast, but, recovering his health, came up to London in October, 1867, with the intention of resuming professional and scientific work. He continued his researches, as regularly as his health permitted, in the laboratory of his brother-in-law, Dr. Edward Dowson, F.C.S., of Park Street. He died at his house at Shepherd's Bush on the 28th of December, 1869, of a very brief illness unconnected with his previous ill-health.

A few words must now be said concerning the scientific work of Mr. Northcote. He published few papers, but everything which he wrote was characterized by minute accuracy and wide research and reading. He never missed any small or obscure phenomenon which presented itself during his experiments, but made it tell its own tale. His last published paper, "On the Water of the Severn," is perhaps the most generally interesting. He considers the influence of the several tributaries of the river upon the constituents of its water, and makes suggestions as to storing it as a water supply when the rainfall is most considerable in those districts which contribute to it the purest water. A list of Mr. Northcote's papers is appended to the present notice.

Mr. Northcote married in 1862 a daughter of Dr. Dowson, of Whitby, in Yorkshire, and leaves three children, two sons and a daughter.

Mr. Northcote gained the affection and esteem of all who knew him. His pupils at Oxford recall his memory with sincere affection. Those friends who were acquainted with him longest and most intimately, feel themselves least able adequately to describe in words his kindliness, his modesty, and the purity and nobleness of his heart and life.

Scientific papers by the late A. B. Northcote, M.A.

1853. "Analytical Notes." Qu. J. Chem. Soc., vi., 54.
1853. "Australian Gold." Phil. Mag. [4] vi., 390.
1855. "On the Function of Salt in Agriculture." Phil. Mag., September.
1855. "On the Brine Springs of Worcestershire." Phil. Mag., January.
1857. "On the Constitution of Allophane." Phil. Mag., May.
1857. "On the Brine Springs of Cheshire." Phil. Mag., December.
1858. "On Thermophyllite." Phil. Mag. [4], xvi., 263.
1864. "On Parathionic Acid." Phil. Mag. [4], xxvii., 218.
1867. "On the Water of the Severn at Worcester." Phil. Mag. [4], xxxiv., 249.

Frederick Penny, Ph.D., F.R.S.E., was born in London on April 10th, 1816, and was the third son of Charles Penny, a prosperous wholesale stationer in Cheapside. At a very early age he suffered, from an accident which affected, not his body only, but probably through it his whole subsequent life, rendering his health delicate, and leading him to a professional rather than a commercial career. His early education was acquired at King Edward's School, Sherborne, in Somersetshire, and at the school of Dr. Lord, in Tooting. From an early age he displayed a liking for chemical pursuits, and his father obtained a place for him, at the age of 14, under Henry Hennell, Esq., F.R.S., chemist of the Apothecaries' Society. For five years, from 1833, he remained in this laboratory as a private pupil; but in 1836 and 1837 he likewise visited the Royal Institution Laboratory, where he obtained additional instruction under Brande and Faraday. During 1837 he attended the lectures on botany of Professor Lindley, and in 1843, after he had settled in Glasgow, he visited Giessen, where he studied for a short time with Liebig.

In 1839, on the 24th January, while the author was in his 22nd year, his first paper was laid before the Royal Society by Mr. Hennell. It was "Upon the application of the conversion of Chlorates and Nitrates into Chlorides to the determination of several equivalent numbers," and was afterwards published in the Philosophical Transactions for 1839. As it has been brought

again before the notice of chemists, by Stas's recent reference to it, it may not be out of place to recapitulate Penny's methods and conclusions. The investigation was commenced by an attempt to find a ready method for estimating the potassic nitrate in crude saltpetre. After some trials, it occurred to him to try the effect of repeated evaporation of the nitrate with excess of hydrochloric acid. Working with specially purified substances, he found that the nitrate was completely converted into chloride; but the quantity of chloride obtained did not agree with the theoretical amount calculated from the combining weights assigned at the time to these salts. In case the discrepancy should have been owing to a fault in the experiments, the converse action, namely, the transformation of potassic chloride into nitrate was tried, and the result agreed almost exactly with that previously obtained. Penny, therefore, considered that the error must exist in the current combining weights, and he now extended his investigation to include oxygen, nitrogen, sodium, and silver. His process consisted in decomposing different compounds, and calculating from those obtained the combining proportions. He thus decomposed potassic chlorate into chloride, not by heat, but by digestion in a flask with hydrochloric acid, and the chloride obtained was in turn converted into nitrate. In the same way the sodic chlorate, nitrate, and chloride were transformed into each other, and the numbers arrived at gave the combining proportions of these salts. He had then recourse to silver compounds, which he transformed in the same way, in order to ascertain the combining weights of potassium, sodium, chlorine, and nitrogen. The equivalents which he assigned to these elements as a result of his experiments are the following:—

Oxygen, 8; chlorine, 35·45; nitrogen, 14·02; potassium, 39·08; sodium, 23·05; silver, 107·97.

The author then proceeded to show that these results lent no support "to the hypothesis of all equivalents being simple multiples of hydrogen."

The simplicity of the experimental method employed and the easy but effectual precautions taken to avoid any error from loss or other accident during the investigation, show that Penny had profited largely by the training he had received, while the systematic statement of his results, and the clearness with which he describes his experiments, indicate the ability

for exposition which was displayed more prominently in his later life. Not the least interesting fact connected with them is that they are confirmed in the most marked manner by the recent determinations of Stas, who has himself pointed out the agreement. For comparison the numbers may be quoted (Fresenius: Zeitschr. für Anal. Chemie. 1868, p. 170):—

	Penny.	Stas.
Chlorine.....	35·45	35·457
Nitrogen	14·02	14·044
Silver.....	107·97	107·930
Potassium.....	39·08	39·137
Sodium	23·05	23·045

It is natural that the author, in re-publishing this research after a lapse of 30 years, should point out with a certain amount of satisfaction the accordance of these results. To this, his first published paper, he was probably a good deal indebted at the outset of his scientific career. It was the best testimonial he could have, as it directed upon him the attention of scientific men. Graham seems to have taken interest in him, and to have given him support in his application for the lectureship in Anderson's Institution, which he himself had left but a year or two before, and which was vacated shortly afterwards by Dr. Gregory. Penny was the successful candidate, being chosen unanimously by the trustees. On his taking possession of his chair, he found that it was not a particularly commodious one. He had to struggle for many years with want of all kinds of teaching and laboratory appliances, besides having to pay a rent to the Institution for the use of rooms. Yet, notwithstanding these and other drawbacks, which he was placed under the necessity of describing towards the end of last year, he relinquished almost entirely his scientific investigations, and devoted his time and energies to the duties of the chair, to teaching, and lecturing. During his first session he enrolled a large number of extra students, and to the very last these numbers, instead of falling off, kept increasing, until he had a very large number of students attending his lectures and laboratory.

As he drew no emolument from the Institution, as the fees from students were at first but small, and there seemed to be some difficulty about the compatibility of his holding the

Andersonian Chair with delivering a course of lectures to other institutions, Penny, who found himself in a large commercial community where chemical science could be turned to good account in connection with the arts and manufactures, took advantage of the opportunity to eke out the scanty income derived from his lectureship. While it may be regretted that he was thus in a manner compelled to abandon pure scientific research, on the other hand the dyers, chemists, iron-masters, miners, metallurgists, and other manufacturers acquired a scientific adviser, whose opinion in course of time came to be highly prized over the whole of Scotland, and especially in Glasgow and the west country. He not only performed numerous analyses of all kinds of commercial products in the laboratory, but his evidence in the law courts was in constant request in many disputes where very large interests were at stake. He was thus engaged in the great Torbanehill case, and his evidence contributed materially to the verdict.

His success as an analyst in poisoning cases caused him to be engaged almost invariably for the prosecution, and the evidence which he gave upon these occasions was so clear, precise, and unwavering, that he was often complimented upon it by the judge. The latest criminal trial in which he was engaged was that of Dr. Pritchard in 1865, and it was on this occasion that he more particularly distinguished himself by his detection of aconite in a quantity of Batley's sedative solution. Not content with chemical tests, he adduced direct physiological evidence that the sedative solution was adulterated, by comparing its effects upon rabbits with pure Batley's solution and with a portion intentionally mixed with aconite.

The papers published by Dr. Penny, after he was fairly involved in consulting commercial practice, when not actual reports upon commercial questions, related chiefly to the composition of several technical products, and accurate methods of testing these, in a form convenient for the technical man.

The year after he left London he published in the "Athenæum," and read to the British Association at its meeting in Glasgow, a paper "On the Action of Nitric Acid upon Chlorates, Bromates, and Iodates," and another "On a New Salt obtained from Iodine and Caustic Soda." In the first paper he shows that the chlorates, thus treated, yield nitrates and perchlorates, with chlorine and oxygen set free; the bromates

yield nitrates only with all the bromine liberated, while the iodates are much more stable, the acid being either simply liberated, or combining with the base to form the well known biniodates.

In the second is described a double salt, $2NaIO_3$. $3NaI$. $19H_2O$, which he prepared by acting on sodic carbonate with iodine, or by crystallising a mixed solution of sodic iodide and iodate. His other papers contain details of the application to volumetric analysis of solutions of potassic anhydro-chromate, a reagent of which he made very considerable use. The process for determining iron, which is called after its inventor—Penny's process—he first described in 1850 to the British Association at its meeting in Edinburgh. It was proposed by Dr. Penny as an easy and accurate method of estimating iron in black-band and clay-band ironstone. The process turns upon the oxidation of the ferrous iron into ferric by the chromic acid, the point at which the change is completed being shown by testing a minute drop of the solution with potassic ferricyanide.

Another application of this reagent which he made was, to estimate tin in the crystallised protochloride, great quantities of which are used by printers and dyers in Glasgow. He determined the composition of the crystals to be $SnCl_2 2H_2O$; he also made an exact experiment to find the precise quantity of bichromate equal to 100 of tin, because the numbers ranged from 83 to 86; he finally settled upon 83·32 as the correct quantity. The action is again that of oxidation, and the end of the operation is ascertained by the precipitation of chromate of lead. He also applied his standard solution to the determination of iodine which is liberated from an iodide by chromic acid in presence of hydrochloric acid, and to estimate the relative value of different samples of indigo. To the British Association he read a description of a method for comparing different qualities of cochineal. The reagent employed was potassic ferricyanide, which bleaches an alkaline solution of the colour.

These, with one or two other papers, were his chief scientific writings, but he is, moreover, the author of a great number of reports, and has left a large mass of recorded experiments and of notes and observations on various topics.

Dr. Penny's health, which had always been delicate, gave way in the latter part of last year, and at the beginning of the

winter session he was suffering from a complication of disorders. He still, however, did his best to carry on his usual lectures, till he was absolutely compelled to give them up. He died on the 22nd of December, 1869.

Otto Linné Erdmann was born at Dresden on the 11th of April, 1804; his father, Carl Gottfried Erdmann, a physician to whom Saxony is indebted for the introduction of vaccination, was a great friend of the natural sciences, especially of Botany, and knew how to arouse a similar inclination in his son, who, during his school days, occupied himself diligently with the collection and classification of plants. In his thirteenth year he left the gymnasium, and was apprenticed to an apothecary, in which position he devoted himself with great ardour to chemistry, making experiments according to his own fancy. This was highly displeasing to his principal, and as Erdmann, by constant standing in the dispensary, had contracted a disease of the foot, he left his place at the end of the second year, in order to resume his studies at the gymnasium, and to prepare himself by private instruction for the study of medicine. This he commenced in 1820 at the Medico-chirurgical Academy in Dresden, and afterwards pursued in 1822 and the following year at the University of Leipzig. It was during this time that the spirited lectures on chemistry, given by Gilbert, professor of physics in the university, aroused Erdmann's former liking for chemistry with redoubled force, so that, when Gilbert died in 1824, he resolved to devote himself for the future exclusively to chemistry. He graduated in the same year, was formally admitted as an academical teacher in 1825, and soon afterwards commenced his lectures, which were received with great interest by the students. In 1826 his academical career was interrupted, circumstances obliging him to leave the university, and undertake the superintendence of a nickel-work in the Hartz; but he gave up this appointment after a year, and resumed his academical functions at Leipzig.

From that time till his death his career was closely connected with the Saxon University. In 1827, when he was only twenty-three years old, he was appointed Extraordinary Professor, and three years afterwards he was invested with the newly created Professorship of Technical Chemistry, which he held for nearly forty years.

His activity as an academical teacher was only once interrupted, namely, in 1836, when he undertook a somewhat prolonged journey, remaining for the longest time at Giessen, then the centre of chemical life in Germany, and at Paris. On his return to Leipzig, he was entrusted by the Saxon Minister of Public Instruction with the preparation of plans for a new laboratory, adapted to meet the requirements of the rapidly advancing science of chemistry, and in 1842 the Laboratorium Friedericianum, built for this purpose, was fitted up according to his directions. It was here that Erdmann carried out the large number of investigations, excepting the earliest, which have given him so honourable a place in the ranks of science.

Erdmann's career as a chemical discoverer commences with an examination of the methods adopted for the preparation and purification of nickel; this research obtained for him the nomination to the Extraordinary Professorship. In his next paper relating to the supposed influence of magnets in inducing chemical decomposition, he shows that the older experiments on this subject were affected with serious errors, and that under the circumstances described by their authors no chemical reaction takes place. These first publications were followed by a series of investigations, chiefly belonging to the field of inorganic chemistry, and relating to analytical questions, or to mineralogy and technology, and including exact analyses of a large number of ores, minerals, and furnace-products. A second and a third memoir on the compounds of nickel are amongst his earlier labours, and to these also is related his last research (1866), on some peculiar double salts of the nitrites of nickel and cobalt with other nitrites.

Erdmann's most important labours belong, however, to two other fields of chemical research, namely, to the investigation of organic compounds, and the determination of atomic weights.

His most important research in organic chemistry relates to indigo. In examining the action of chlorine and bromine on indigo-blue, he discovered two compounds derived from isatin, the member of the indigo group which has formed the starting point of all subsequent investigations relating to this colouring matter. After he had prepared a whole series of chlorinated and brominated derivatives of isatin, he succeeded, simultaneously with Laurent, in obtaining that body itself,

and to him undoubtedly belongs the merit of having given, by his earlier investigations, the impulse to this discovery. In his first memoirs, however, partly in consequence of the too high atomic weight of carbon then generally adopted, partly from not expelling the oxygen from his potash-bulbs before weighing, Erdmann did not arrive at the true formulæ of the compounds which he examined; but it is greatly to his honour that when Laurent pointed out the errors of his formulæ, he at once admitted them, and helped by new analyses to correct his earlier statements.

The same investigations led him to the discovery of chloranil and chloranilic acid, compounds which have since formed the starting point of the quinone group, and have furnished an explanation of the constitution of this class of bodies.

This greatest of Erdmann's labours in the field of organic chemistry was followed by several smaller researches, among which we may specify those upon euxanthic acid, hæmatoxylin, and mellitic acid. The investigation of this last-mentioned body made us acquainted with the first, and till lately the only known quadribasic organic acid.

Erdmann's acquaintanceship with Marchand, made during his journey in 1836, led to results of the highest value for chemical science in the exact determination of atomic weights. To appreciate the value of the results obtained by these chemists, it is sufficient to observe that the numbers at which they arrived are still in use, and that their exactness has in every case been fully confirmed by more recent investigations.

Dumas and Stas in 1841 showed that the number 76·43 (O = 100) adopted up to that time as the atomic weight of carbon, was incorrect, and deduced from their own experiments the number 75. Berzelius did not adopt this alteration, but endeavoured by new analyses to defend the old number. This controversy, and the great importance attached to its decision, induced Erdmann and Marchand to examine the statements of the French chemists, and they began their investigations not without doubts as to the correctness of the new number; but an extremely conscientious and thorough repetition of the experiments of Dumas and Stas, led to results which completely established their exactness.

By a comparison of the experiments made during this investigation with the principles on which the greater number of

equivalent numbers then generally adopted had been calculated, Erdmann and Marchand became convinced of the necessity of a thorough revision of the atomic weights of all the elementary bodies. To this labour they devoted themselves with the greatest energy, till the death of Marchand, in 1850, put an end to their joint investigations.

Simultaneously with Dumas they found for the ratio of the atomic weights of hydrogen and oxygen the value 1 : 8, and for calcium the number 250 (O=100). They also determined the true atomic weight of mercury, sulphur, and iron, which till then had not been correctly ascertained. These investigations, however, did not go on without controversy. Berzelius hesitated to adopt the new numbers, because they did not agree with his own older analyses, and because they afforded fresh support to Prout's law, to which he was violently opposed; he therefore pronounced decidedly against the numbers obtained by Erdmann and Marchand. These chemists were accordingly compelled to publish a reply, in which they demonstrated the groundlessness of the objections urged by the great Swedish chemist. But to all who examined the question impartially, this reply was unnecessary, and the numbers determined by Erdmann and Marchand quickly obtained universal acceptance.

Erdmann was also an industrious chemical writer. In 1828 he published his "Lehrbuch der Chemie," which was very favourably received, and went through four editions, the last of which was published in 1851. Soon after the publication of the first edition, he founded his "Journal für technische und ökonomische Chemie" (18 vols.), followed in 1834 by the "Journal für praktische Chemie," which he edited, first alone, afterwards in conjunction with Schweigger-Seidel and Marchand, and since 1853 with Werther. His acquaintance with technology he applied to the compilation of a "Grandriss der Waarenkunde," which first appeared in 1834, and attained its sixth edition in 1868.

As a teacher, Erdmann was universally admired. His style was clear and a model of eloquence, and his explanations were elucidated by well chosen and admirably performed experiments: he possessed also in a rare degree the power of interesting a general audience in the facts and principles of his science. He was equally successful as a director of the labora-

tory, knowing well how to impart his own exactness and conscientiousness in work to his students.

He, moreover, filled with the highest efficiency the honorary positions which were from time to time conferred upon him by the university; and in his capacity of Rector, under the difficult circumstances of the years 1848 and 1849, he succeeded in gaining the esteem of the whole body of students.

In speaking of a man of Erdmann's many-sidedness and varied cultivation, we must not conclude without a glance at his relations in civic and social life. In the public affairs of his country and of the town of Leipzig, he took the greatest interest. In 1835 he was elected a Director of the Leipzig and Dresden Railway, an office which he discharged with the greatest efficiency, and, ultimately as Chairman, to the close of his life. In this position also he found an opportunity of turning his chemical knowledge to account. Several attempts had been made on this railway to replace the English coke, which leaves but a small amount of ash, by Saxon coke; but all these attempts had failed, partly on account of the large amount of earthy constituents in the Saxon coal, partly because it is mostly mixed with pyrites. Erdmann showed, however, that it may be made available by mixing it, before coking, with a quantity of slaked lime proportioned to its amount of ash. The coke thus obtained yields an ash which melts and runs down at the heat of the furnace. The lime also serves to render the sulphur innocuous.

Erdmann was also Chairman of the Committee of the Leipzig Life Assurance Company, President of the Harmonic Society, and of the Leipzig Art Union, and the author of several papers relating to art. He always enjoyed excellent health, till late in the summer of 1868, when he was attacked with inflammation of the pericardium, and so violently that his condition gave but little hopes of recovery. Quite unexpectedly, however, an improvement soon took place, so that in the following winter he was able to resume his work, and in the spring of 1869 his health appeared to be quite re-established. But this improvement was of short duration, for in the following July his disorder (dropsy of the pericardium) set in with renewed violence, and in a short time all hope of recovery vanished. On the 9th of October, at the age of $65\frac{1}{2}$, he was relieved from his severe sufferings by death.

Joseph Redtenbacher was born at Kirchdorf, in Upper Austria, on the 12th of May, 1810. His father, who was a merchant, gave him a careful education, first at the Stiftsgymnasium of Kremomünster, afterwards at the University of Vienna. In 1834 he took his degree of Doctor of Medicine, and soon afterwards became assistant to Baron Taquin, professor of chemistry and botany. After passing his examination as a teacher, he went (1838) as professor to the Chirurgical Academy at Salzburg, received a travelling fee, and visited the University of Giessen, where he worked with Liebig, and became acquainted with Bunsen, Hofmann, Stenhouse, Kopp, and other chemists.

After his return he was made junior professor at the University of Prague, and in 1849 he was summoned to the High School of Vienna, where he worked till his death, which took place on the 5th of March, 1870.

Amongst his researches the following may be enumerated in chronological order :—

1840. "Investigation of Methionic Acid.—On the composition and distillation-products of Stearic and Sebacic Acids."
1841. "Researches on Felspar.—Determination of the atomic weight of Carbon (with Liebig)."
1843. "On the decomposition of Glycerin (discovery of Acrolein)."
1846. "On the action of Nitric Acid on Dyslysin and Cholesterin, and on the composition of Taurine."
1848. "New mode of formation of Metacetonic Acid.—On the Acid in the fruit of *Ceratonia Siliqua* (St. John's bread)."
"On a General Mode of Formation of the Fatty Acids, $C^nH^nO^4$, boiling below 300° C."
1848. "On the Constitution of Taurine, and on Acid Sulphite of Aldehyde-ammonia."

List of Papers read at the meetings of the Chemical Society between March 30th, 1869, and March 30th, 1870 :—

1. "On some Decompositions of Acids of the Acetic Series:" by E. T. Chapman and Miles H. Smith.
2. "On Coumaric Acid:" by W. H. Perkin, F.R.S.

3. "On Propyl Compounds derived from the Propylic Alcohol of Fermentation:" by E. T. Chapman and Miles H Smith.
4. "On Bromide of Amyl:" by E. T. Chapman and Miles H. Smith.
5. "On the Atomicity of Sodium:" by J. A. Wanklyn.
6. "On the Constitution of Hyposulphurous Acid:" by C. Schorlemmer.
7. "On Sulphate of Alumina from Iquique, Peru:" by F. Field, F.R.S.
8. "On Regnault's Chlorinated Chloride of Methyl:" by W. H. Perkin, F.R.S.
9. "On Ethyl-hyposulphurous Acid:" by R. H. Smith.
10. "Note on the Absorption-Spectra yielded by certain Organic Substances:" by T. L. Phipson.
11. "Researches on the Constitution and Reactions of Tyrosine:" by Dr. Thudichum and J. A. Wanklyn.
12. "Note on Oxalate of Silver:" by Dr. Thudichum and J. A. Wanklyn.
13. "Note on Dumas' Method of Determining Nitrogen:" by Dr. Thudichum and J. A. Wanklyn.
14. "On the Atomic Weight of Cobalt and Nickel:" by W. J. Russell.
15. "On Chlorhydrated Sulphuric Acid:" by the Rev. Stephen Williams.
16. "On an Apparatus for determining the quantities of Gases existing in solution in Natural Waters:" by Herbert McLeod.
17. "On a New Form of Apparatus for Gas Analysis," by Herbert McLeod.
18. "On Ethylbenzoic Acid:" by A. Kekulé and T. E. Thorpe.
19. "On the Products of the Action of Nitric Acid on the Resinous Extract of Indian Hemp:" by Thomas Bolas and E. H. Francis.
20. "On the Formation of Carbonic Ether:" by W. Dittmar, and Geo. Cranston.
21. "On the Dissociation of liquid Sulphuric Acid:" by W. Dittmar.
22. "On Namaqualite:" by Prof. Church.
23. "Chemical Researches on New and Rare Cornish Minerals:" by Prof. Church.

24. "On Chloranil and Bromanil:" by Dr. Stenhouse, F.R.S.
25. "On the Salts of Acetylinated Ethyl:" by J. A. Wanklyn.
26. "Remarks on some points in the Nomenclature of Salts:" by H. G. Madan.
27. "Results of the Analysis of Sea-water, performed on board H.M.S. 'Porcupine,' July 1869:" by John Hunter.
28. "On the Absorption of Mixed Vapours by Charcoal:" by John Hunter.
29. "On the Composition of Iron Rust:" by Dr. Crace Calvert, F.R.S.
30. "On the Organic Matter contained in Air:" by E. T. Chapman.
31. "On some Reactions of Alcohols:" by E. T. Chapman.
32. "Experiments illustrating Berthelot's formation of Hydrocyanic Acid from Free Nitrogen and Acetylene:" by W. H. Perkin, F.R.S.
33. "On the Action of Light upon Vapours:" by Professor Tyndall.
34. "On Kryptophanic Acid:" by Dr. Thudichum.
35. "On Artificial Alizarin:" by W. H. Perkin, F.R.S.

The following lectures have also been delivered:—

"On the Chemistry of the Blast Furnace:" by J. Lowthian Bell.
"On the Atomic Theory:" by Dr. Williamson.
"On Refraction Equivalents:" by Dr. Gladstone.

The inaugural Faraday Lecture was also delivered by M. Dumas.

The following Fellows were elected Officers and Council for the ensuing year:—

President.—A. W. Williamson, Ph.D., F.R.S.

Vice-Presidents who have filled the office of President.—Sir B. C. Brodie, F.R.S.; Warren De La Rue, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; W. A. Miller, M.D., D.C.L., F.R.S.; Lyon Playfair, Ph.D., C.B., F.R.S.; Colonel P. Yorke, F.R.S.

Vice-Presidents.—J. H. Gilbert, Ph.D., F.R.S.; E. Frankland, Ph.D., F.R.S.,; A. Matthiessen, Ph.D., F.R.S.; H. M.

Noad, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; T. Redwood, Ph.D.

Secretaries.—A. Vernon Harcourt, M.A., F.R.S.; W. H. Perkin, F.R.S.

Foreign Secretary.—Hugo Müller, Ph.D., F.R.S.

Treasurer.—F. A. Abel, F.R.S.

Other members of the Council.—E. Atkinson, Ph.D.; H. Bassett; E. T. Chapman; F. Field, F.R.S.; David Forbes, F.R.S.; M. Holzmann, Ph.D.; E. J. Mills, D.Sc.; W. J. Russell, Ph.D.; Maxwell Simpson, M.D., F.R.S.; R. Angus Smith, Ph.D., F.R.S.; John Tyndall, LL.D., F.R.S.; A. Voelcker, Ph.D.

Dr. The Treasurer in Account with the Chemical Society from March 25, 1869, to March 26, 1870. Cr.

	£ s. d.	£ s. d.
Balance in hand, March 26th, 1869		586 15 1
Dividends on £2,700 Consols		79 6 4
Mathematical Society for gas and fire at Meetings		1 10 0
Sale of Journals		50 0 3
Sundry Receipts from 25th March, 1869, to 25th March, 1870.		
41 Admission Fees	82 0 0	
8 Life Compositions	168 0 0	
1 Subscription for 1867	2 0 0	
17 Subscriptions for 1868	27 0 0	
88 ditto for 1869	153 0 0	
346 ditto for 1870	616 0 0	
		1048 0 0
		£1765 11 8

Assets.	£ s. d.
Balance at Coutts'	953 10 0
Three per Cent. Consols	2700 0 0

	£ s. d.	£ s. d.
Expenses on Account of Journal.		
Editor's Salary	95 0 0	
Printing Journal, and Provision of Author's Copies of Papers	237 13 1	
Distributing Journals..	52 17 3	
		385 10 4
Preparation of Reports of Meetings		34 10 9
Proceedings of the Royal Society		50 0 0
Expenses on Account of Library.		
Salary of Librarian	25 0 0	
Books and Periodicals—English and Foreign	30 6 2	
Binding of Books and Periodicals	24 11 9	
Gratuity to Librarian for preparation of new Catalogue and arrangement of Pamphlets	15 0 0	
		94 17 11
Collector's Commission on Subscriptions and Treasurer's Receipt Stamps	1 7 10	
		53 13 10
Clerical Expenses		5 0 0
Stationery and Stamps		23 16 4
Expenses connected with the Faraday Medal and Faraday Lecture for 1869.		
To Mr. Owen Jones for a design for the Reverse of the Medal	10 10 0	
To Mr. L. E. Wyon in part payment for preparation of the dies of the Medal	52 10 0	
Fittings provided in the Theatre of the Royal Institution on the occasion of the Faraday Lecture	4 17 0	
Stationery, Admission Cards, Circulars, and Postage	9 11 5	
Honorarium presented to the Faraday Lecturer	20 0 0	
		97 8 5
House Expenses.		
Provision of Tea, &c., at the Meetings	16 3 11	
Gas and Lamps for Meeting Rooms	7 5 6	
Coals	2 7 0	
Salary of House Porter	20 0 0	
Special Gratuity voted to the late House Porter	10 0 0	
Hall Porter—Annual Gratuity	2 2 0	
Petty Expenses	9 6 3	
		67 4 8
Balance at Messrs. Coutts'		953 10 2
		£1765 11 8

April 7th, 1870.

The following gentlemen were duly elected Fellows of the Society:—

Thos. Andrews, Jun., Wortley Iron Works, Sheffield; William Martindale, University College Hospital, London; Alfred N. Palmer, Bury St. Edmunds, Suffolk.

The following papers were read:—

"On the analysis of Deep Sea Water:" by Mr. John Hunter, M.A.

"On the Refraction Equivalents of the Aromatic Hydrocarbons and their Derivatives:" by Dr. J. H. Gladstone.

"On Bromopicrin:" by Messrs. Thomas Bolas and C. E. Groves.

"On an Acid Feed-water from the Coalfields of Stellarton, N.S., and the results of its Use:" by Prof. Howe.

April 21st, 1870.

Dr. Williamson, President, in the Chair.

The following gentleman was duly elected a Fellow of the Society:—

Isaac Patchett, Birstall, near Leeds.

A lecture on Vanadium was delivered by Prof. Roscoe.

Dr. A. W. Hofmann made some remarks upon a new substance obtained by treating Sulphur-urea with Silver-oxide.

May 5th, 1870.

Dr. Williamson, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

Geo. Matthey, Hatton Garden; James Steel, 103, St. Vincent Street, Glasgow; John Allen, Phœnix Chemical Works, Bow Common.

The following papers were read:—

"On Vapour-Densities:" by Mr. J. T. Brown.

"On Restormelite and Chalcophyllite:" by Prof. Church, M.A.

"On Tetrabromide of Carbon:" by Messrs. Thomas Bolas and C. E. Groves.

May 19th, 1870.

Dr. Warren De la Rue, Vice-President, in the Chair.

The following gentleman was duly elected a Fellow of the Society:—

Samuel H. Johnson, Alton Eloick, Hamfrith Road, Stratford.

The following papers were read:—

"On a New Gas Furnace:" by Mr. Griffin.

"On the Manipulation of Assays of Gold and Silver:" by Mr. Tookey.

"On some Bromine-derivatives of Coumarin:" by Mr. W. H. Perkin.

"On the Precipitation of Solution of Ammonium Carbonate, Sodium Carbonate, and Ammonium Carbamate, by Calcium Chloride:" by Dr. Divers.

"On the Acids contained in Urine:" by Dr. Thudichum.

June 2nd, 1870.

Dr. Williamson, President, in the Chair.

The following gentleman was duly elected a Fellow of the Society:—

W. B. Lustin, 9, Paragon, Blackheath.

A lecture on the Platinum Ammonias, was delivered by Prof. Odling.

June 16th, 1870.

Dr. Williamson, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

A. W. Bickerton, Hartley Institution, Southampton; Louis Arthur Lucas, 46, Westbourne Terrace, Hyde Park.

The following papers were read:—

"On Fermentation:" by Mr. Bell.

"On the Organic Matter in Water;" by Dr. Heisch.

"On the Determination of Carbon in Steel:" by Mr. W. D. Herman.

Donations to the Library, 1868–69.

"Notes on French Government Manufactories of Gunpowder, Percussion-caps, &c., submitted to the Secretary of State for War:" by F. A. Abel: from the Author.

"Preliminary Report to the Secretary of State for War from the Government Commission on Explosive Agents:" from F. A Abel, Esq.

"Chemistry, General, Medical, and Pharmaceutical:" by John Attfield: from the Author.

"On the Development and Appropriation of Heat in Iron Blast Furnaces of different dimensions:" by J. Lowthian Bell: from the Author.

"The Student's Chemistry:" by A. J. Bernays: from the Author.

"Patent Monopoly and Statistics of Invention:" four Pamphlets: by H. Dircks: from the Author.

"Ganot's Elementary Physics:" translated by Dr. E. Atkinson: from Messrs. Longman and Co.

"On the Sulphur Acids of Benzol:" by A. Ross Garrick: from the Author.

"Contributions to Chemistry from the Laboratory of the Lawrence School, Harvard University. On the Action of the Alkalies on Uric Acid and its derivatives: by Wolcott Gibbs: from the Author.

"On Phosphorus Compounds:" by J. H. Gladstone: from the Author.

"On Hydrofluoric Acid:" by G. Gore: from the Author.

'Exercises in Practical Chemistry:" by A. G. Vernon Harcourt and H. G. Madan; Series I: from the Authors.

"On the Terraces of Norway:" by Professor Kjerulf: from the Author.

"Elements of Chemistry:" by W. A. Miller." Fourth Edition of Part III: from the Author.

"A Sketch of a Philosophy, Part IV. The Chemistry of Natural Substances:" by J. G. Macvicar: from the Author.

"On the Structural Relations of Urea and Uric Acid:" by J. G. Macvicar: from the Author.

"Outlines of Chemistry:" by William Odling: from the Author.

"Le Préparateur Photographe:" par T. L. Phipson: from the Author.

"Meteors, Aerolites, and Falling Stars:" by T. L. Phipson: from the Author.

"The Utilisation of Minute Life:" by T. L. Phipson: from the Author.

"Spectrum Analysis," Second Edition: by H. E. Roscoe: from the Author.

"The Royal Society's Catalogue of Scientific Papers," Part III: from the Royal Society.

"Salter's Edition of Field's Chromotography:" from the Editor.

"On Colophonic Acid and Colophonic Hydrate:" by C. R. C. Tichborne: from the Author.

"Veterinary Pharmacopœia:" by R. V. Tuson: from the Author.

"Fresenius' Quantitative Analysis:" edited by A. Vacher: from the Author.

"On Beetroot Pulp:" by A. Voelcker: from the Author.

"Field Experiments on Mangolds:" by A. Voelcker: from the Author.

"On the Development of Agricultural Chemistry:" by A. Vogel: from the Author.

"Outlines of Crystallography:" by P. Waage and H. Mohn: from the Authors.

"Abridgments of Specifications relating to Aeronautics:" compiled by W. H. Walenn: from the Compiler.

"On the Absorptive power of Soil:" by Robert Warington: from the Author.

"On the Atomic Theory:" by Professor Williamson: from the Author.

"De L'Influence de l'Eau sur les Doubles Décompositions:" par C. Marignac: from the Author.

"Sull' Ozone—Note e Reflessioni:" di Giuseppe Bellacci: from the Author.

"Ueber den Molecular-Zustand des Zinns:" von J. Fritzsche: from the Author.

"Fatti per servire alla Determinatione del Luogo Chimico delle Sostanze Aromatiche:" di W. Koerner: from the Author.

"Denkschrift an C. F. von Martius:" von G. Meissner: from the Royal Bavarian Academy of Sciences.

"Ueber die Ueberjodsäure und ihre Salze:" von C. Rammelsberg: from the Author.

"Die Schule der Chemie: von Dr. Julius Adolph Stockhardt: from the Author.

Periodicals:—

"Philosophical Transactions," 1868, Part II: from the Royal Society.

"List of Officers and Fellows of the Royal Society for 1869:" from the Royal Society.

"Proceedings of the Royal Institution of Great Britain," 1869: from the Royal Institution.

"List of Members, Officers, and Professors of the Royal Institution for 1870:" from the Royal Institution.

"Quarterly Journal of Science," 1869–70: from the Editor.

"Journal of the Photographic Society," from June, 1869 to May, 1870: from the Society.

"Pharmaceutical Journal and Transactions," from June, 1869, to June, 1870: from the Pharmaceutical Society.

"Journal of the Society of Arts," 1869–70: from the Society.

"Chemical News," 1869–70: from the Editor.

"The Chemist and Druggist," from July, 1869, to June, 1870: from the Editor.

"Monthly Notices of the Royal Astronomical Society," from November, 1869, to June, 1870: from the Society.

"Quarterly Journal of the Geological Society," 1869–70: from the Society.

"Nature: a weekly illustrated Journal of Science," Parts 1 to 32: from the Editor.

"Engineering," from July, 1869 to June, 1870: from the Editor.

"Scientific Opinion," Nos. 62 to 84: from the Editor.

"Fortieth Annual Report of the Royal Cornwall Polytechnic Society," 1869: from the Society.

"Annual Report of the Leeds Philosophical and Literary Society," 1868, 1869: from the Society.

"Proceedings of the Literary and Philosophical Society of Liverpool:" from the Society.

"Memoirs of the Literary and Philosophical Society of Manchester," Vol. III, 1868: from the Society.

"Proceedings of the Literary and Philosophical Society of Manchester," Vols. V, VI, VII: from the Society.

"Transactions of the Newcastle-on-Tyne Chemical Society," 1868–69: from the Society.

"Transactions of the Royal Society of Edinburgh," Vol. XXXV, Part 2, 1868–69.

"Proceedings of the same, Session," 1868–69: from the Society.

"Proceedings of the Philosophical Society of Glasgow," 1869: from the Society.

"Journal of the Chemico-Agricultural Society of Ulster," No. 6: from the Society.

"American Journal of Science and Arts," from July, 1869, to May, 1870: from the Editor.

"Journal of the Franklin Institute," from May, 1869, to May, 1870: from the Institute.

"Transactions of the American Philosophical Society," 1869: from the Society.

"Proceedings of the American Philosophical Society for 1867, 1868, and 1869:" from the Society.

"Proceedings of the Academy of Natural Sciences at Philadelphia," 1869, Parts 1 to 6: from the Academy.

"Report of the Commissioner of Agriculture for the year 1867, Washington:" from the Commissioner.

"Report of the National Academy of Sciences at Washington:" from the Smithsonian Institution.

"Annual Report of the Board of Regents of the Smithsonian Institution:" from the Institution.

"Monthly Report of the Deputy Special Commissioner of the Revenue (United States)," March, 1869: from the Commissioner.

"Annual Reports of the Commissioner of Patents (United States)," 1867, Vols. I—IV: from the Commissioner.

"Transactions of the Royal Society of New South Wales," Vol. I: from the Society.

"Archives Néerlandaises," Tome IV, 1869: from the Editor.

"Bulletin de l'Académie Impériale des Sciences de St. Petersbourg," Tomes XIII, XIV: from the Academy.

"Bulletin de l'Académie Royale de Belgique," Tomes XXVII., XXVIII.

"Annuaire de l'Académie Royale de Belgique," 1869: from the Academy.

"Cosmos," Tomes V, VI: from the Editor.

"Moniteur Scientifique," 1869: from the Editor.

"Revue des Cours Scientifiques," Nos. 1—20: from the Editor.

"Memoire dell'Accademia delle Scienze dell'Istituto di Bologna," Tomi VII, VIII: from the Academy.

"Rendiconti delle Sessioni dell'Accademia delle Scienze dell' Istituto di Bologna," 1867–68 e 1868–69: from the Academy.

"Giornale di Scienze naturali ed economiche, publicato per cura del Consiglio di Perfezzionamente annesso al R. Istituto tecnico di Palermo," 1869: from the Institute.

"Berichte der deutschen Chemischen Gesellschaft zu Berlin," 1869–1870: from the Society.

"Monatsberichte der Königlichen Akademie der Wissenschaften zu Berlin," 1869–1870: from the Academy.

"Denkschriften der Kaiserlichen Akademie der Wissenschaften zu Wien," Band XXIX: from the Academy.

"Sitzungsberichte derselben," Bände LVIII, LIX, LX: from the Academy.

"Sitzungsberichte der Königl.-bäyrischen Akademie der Wissenschaften zu München," 1869; Bd. I., Heft. 4; Bd. II., Hefte 1—4; 1870, Bd. I., Heft 1: from the Academy.

"Zeitschrift für Chemie," 1869–1870: from the Editor.

"Vierteljahrsschrift der Naturforschenden Gesellschaft in Zürich," 8 Hefte, für 1867 and 1868: from the Society.

"Oefversigt af Kongl. Vetenskaps Akademiens Forhandlingar," 1866–1868: from the Royal Academy of Sciences at Stockholm.

"Oversigt over det Kongelige Danske Viderskabernes Selskabs Forhandlinger, og dets Medlemmers Arbeeten," 1869: from the Royal Danish Academy of Sciences.

XXV.—*On Vapour-Densities.*

By Jas. T. Brown.

When I first thought of publishing these Tables, which I now have the honour of bringing before this Society, I intended to place as an introduction to them merely the formulæ of the various vapour-density methods without note or comment, but I found that, owing to the impossibility of giving to the letters used the same significance in all the formulæ, I should, by so doing, only be adding to the difficulty of a subject which is, in some parts, rather complicated. I therefore propose to give as short a sketch as possible of the different methods, confining my remarks to the characteristic points in each, and giving the various formulæ in the shape best adapted for calculation by the aid of the accompanying tables which indicate the values of the principal terms employed in the formulæ, viz., $\frac{0{\cdot}0012932}{760(1 + 0{\cdot}00367T)}$, $\frac{0{\cdot}0012932}{760(1 + 0{\cdot}00367t)}H$ and also $\frac{1 + 0{\cdot}00367T}{1 + 0{\cdot}00367t}$, and their logarithms and log. $(1 + k(T - t))$. These processes may all be classed as modifications of one or other of two methods, viz., Gay-Lussac's or Dumas'; in the former the weight of substance employed is known, and the volume which it occupies under certain conditions is to be determined; in the latter the volume occupied by the vapour is known, and the weight is to be determined.

The apparatus generally described for the determination of a Gay-Lussac vapour-density consists of a graduated tube, which is held in an upright position in a large vessel of mercury, and is heated by being surrounded with hot water contained in a glass cylinder, open at both ends, which dips into the mercury, so that the column of water in the cylinder is balanced by the mercury in the outer vessel. By this method, which is only available up to 100°, we have the Gay-Lussac formula in its simplest form:—

Let P = weight of substance employed.
T = temperature of water in cylinder.
H = height of the barometer (corrected).

t = atmospheric temperature.
h = height of mercury in graduated tube above mercury in outer vessel.
h'' = tension of mercury vapour.
V = volume of vapour.
k = co-efficient of expansion of glass.

The formula then becomes—

$$D = \frac{P}{\frac{0{\cdot}0012932}{760\,(1+0{\cdot}00367\,T)}\,V\,(1+k\,(T-t))\,\left(H-\frac{h}{1+0{\cdot}00018\,T}-h''\right)}$$

The calculation of the result by natural numbers is much simplified by using tables published in Vol. 4, N. S. of this Society's Journal;* but if we avail ourselves of logarithms the calculation is rendered still easier with the help of the accompanying tables. As the same expressions occur repeatedly in the various formulæ we will use the following abbreviations:—

Let $\frac{0{\cdot}0012932}{760(1+0{\cdot}00367\,T)} = \alpha$
and $(1+k\,(T-t)) = \beta$
and H' = total corrected pressure on vapour.
Then $\log. D = \log. P - \log. \alpha - \log. V - \log. \beta - \log H'$.

The modification of Gay-Lussac's method proposed by Natanson† consists in heating the upper part of the graduated tube in an air-bath by means of charcoal, the temperature being indicated by a thermometer placed close to the graduated tube. As this process may be used at any temperature up to 300°, the correction for the tension of mercury vapour is essential.

Hofmann‡ uses a graduated tube of a metre in length (so that, before the introduction of the substance, there is a Torricellian vacuum above the mercury), surrounds the upper part of it with a larger tube, and heats it by means of steam or the vapour of any liquid which has a constant boiling point. He also prefers to use small stoppered bulbs for the substance instead of sealed ones.

Wichelhaus's§ modification of Hofmann's method consists in connecting to the bottom of the graduated tube a small tube

* Journ. Chem. Soc., new series, 4, 72.
† Ann. Chem. Pharm. 98, 301.
‡ Berichte d. D. Chem. Gesellschaft, 1, 198.
§ Ibid., 3, 166.

bent upwards, so that the vessel of mercury may be dispensed with, and the whole tube may be inserted in the steam-bath.

For Gay-Lussac's determinations at any temperature up to 150°, a very convenient modification has been proposed by Greville Williams.* It consists in replacing the large vessel of mercury and the open glass cylinder by a cylinder closed and rounded at the lower extremity so as to resemble a large test-tube.

This is then filled to a depth of 50—60 mm. with mercury, and above that with water or oil to a convenient height. The graduated tube is filled and the bulb inserted over the mercurial trough; it is then immersed in the large tube by means of a rod, having at the end a small cup containing mercury. The large tube may be supported on wire gauze and heated by a Bunsen burner, or it may be heated, preferably, supported in a shallow oil-bath. The formula for this method is the same as that previously given, except that the column of water or oil, as the case may be, must be taken into account and its value in millimetres of mercury added to the pressure. In the case of water the calculation will be avoided by referring to a table given in Bunsen's Gasometry.† In using oil, its average specific gravity may be taken at 0·92, and its co-efficient of expansion at 0·0008, so that the pressure of a column h of oil at a temperature T will be $\frac{h(0{\cdot}92)}{13{\cdot}59(1 + 0{\cdot}0008T)}$, which at 100° = 0·0627$h$, and at 150° = 0·0604$h$.

In order to determine vapour-densities under increased pressure, some alterations in detail are required, although the principle is the same as are the processes already described. In Greville Williams'‡ method the graduated tube is, after it has been filled and the bulb has been inserted, screwed by means of a nipple cemented to the bottom, into an orifice in the top of a small metallic cistern into a second orifice in which a long open glass tube is fitted. Into this tube mercury is poured until the required pressure is obtained. If it is wished to reduce the pressure, the excess of mercury is allowed to escape by a tap in the side of the cistern. The whole is heated by being immersed in a water- or oil-bath.

In Regnault's§ apparatus for accomplishing the same object

* Watts' Dict. Chem., 5, 367.
† Bunsen's Gasometry, 285.
‡ Williams, Chem. Manip., 542.
§ Ann. Chim. Phys, 3rd series, 63, 45.

the two tubes are fastened to the bottom of the water-bath, and are connected underneath by a T-piece which is closed by a three-way cock of peculiar construction. The formula for this method is the same as the typical Gay-Lussac formula already given, but care must be taken to place the right sign before the quantity $\frac{h}{1 + 0{\cdot}000187T}$, as it will be positive or negative, according to circumstances.

If it is desired to determine a vapour-density at a temperature near the boiling point of the substance, it is advisable to employ a method which was proposed by Regnault,* and simultaneously by Playfair and Wanklyn†. It consists in admitting into the graduated tube a certain volume of air or any permanent gas before heat is applied. By this means the vapour is less liable to condensation, and obeys the law of permanent gases more nearly than it would otherwise.

Then if P be the weight of substance employed,
and V be volume of gas at temperature t and pressure H,
and V' be the volume of gas and vapour at temperature T and pressure H',

$$\text{then } D = \frac{P}{V'\frac{0{\cdot}0012932}{760\,(1 + 0{\cdot}00367T)}H' - V\frac{0{\cdot}0012932}{760\,(1 + 0{\cdot}00367t)}H}$$

$$= \frac{P}{V'a\,H' - V\,a\,H}$$

In all the methods hitherto described, the result depends to a great extent on the accuracy of the thermometer, by means of which the temperature during the experiment is determined; but in the method proposed by Grabowski,‡ many errors are eliminated, and the only thermometer required is one capable of indicating atmospheric variations of temperature. The process is conducted in the following manner:—By the side of the graduated tube, in which the substance is heated by means of gas in an air-bath specially constructed for the purpose, is placed another graduated tube, of the same length and same capacity, filled with mercury. As soon as the substance is all converted into vapour, air is passed up into the second tube

* Ann. Chim. Phys., 3rd series, 63, 45.
† Trans. Roy. Soc. Edin., 22, Part 3, 441.
‡ Sitzungsber. d., Akad. z. Wien., 53; Abth., 2, 84.

until it occupies as nearly as possible the same volume as the vapour. The vapour and air are therefore at the same temperature under similar conditions and at nearly the same pressure. The volume V and pressure H of the air, and the volume V' and pressure H' of the vapour are observed, and the apparatus is allowed to cool in order that the weight of the air employed in the experiment may be determined by measuring the volume v, which it occupies at the atmospheric temperature t, and at the pressure H'', then if P be weight of substance employed,

$$D = \frac{P\,V\,H}{v\,\frac{0{\cdot}0012932}{760\,(1+0{\cdot}00367t)}\,H''\,V'\,H''} \text{ or very nearly } = \frac{P}{v\,\frac{0{\cdot}0012932}{760\,(1+0.00367t)}\,H''}$$

$$= \frac{P\,V\,H}{v\,a\,H''\,V'\,H'} \text{ or very nearly } = \frac{P}{v\,a\,H''}$$

The modification proposed by Dr. W. M. Watts* consists in heating the substance, which has been weighed in a small bulb, in a globe, into the neck of which is ground a glass tube, reaching nearly to the bottom of the globe, to serve as an exit for the mercury expelled by the vapour. The volume occupied by the vapour is then calculated from the weight of mercury thus expelled, taking into consideration the capacity of the globe and the temperature during the experiment.

Then if W = weight of mercury which fills globe at $t°$,
and W' = weight of mercury expelled by vapour,

and if the other letters have the same signification as in the previous formulæ—

$$\text{then D} = \frac{P}{\left[V\left(1+k\,(T-t)\right) - \frac{W-W'}{13{\cdot}59}\left(1+0{\cdot}00018\,(T-t)\right)\right]\frac{0{\cdot}0012932}{760(1+0{\cdot}00367\,T)}\left(H+\frac{h}{1+0{\cdot}00018\,T}-h\right)}$$

$$= \frac{P}{\left[V\beta - \frac{W-W'}{13{\cdot}59}\left(1+0{\cdot}00018\,(T-t)\right)\right]a\,H'}$$

In using this method, it is important that the exit-tube should not be too small, otherwise the effect of capillarity will be to cause a perceptible increase in the pressure on the vapour.

* Laboratory, 1, 225.

Dumas' method, modified according to circumstances, may be used for the determination of the vapour-density of any substance boiling below a red heat, but the quantity of material required is much larger than in determinations by Gay-Lussac's method. In its ordinary form, which is available at any temperature up to 250°, the process is conducted as follows:—A globe of easily fusible glass, of a capacity of 100–200 cc., and provided with a neck which terminates in a fine point, is carefully weighed full of dry air. A portion of the substance is then introduced and the bulb heated, with the point projecting, in an oil-bath to 30 or 40° above the boiling-point of the substance; the point is then sealed and the bulb is allowed to cool, and, after being cleaned, is weighed. The temperature of the balance-case, and the height of the barometer are then noted. The bulb is then held neck downwards, partly immersed in mercury, and the point is broken off. If, as is generally the case, the mercury does not completely fill the globe, the volume of the residual air must be determined; the quickest method is that proposed by Greville Williams,* viz., to measure by means of a burette the quantity of mercury which is required to displace the bubble of air. The capacity of the globe is ascertained by measuring the mercury required to fill it. Deville and Troost† recommend determining the capacity of the globe and the volume of the residual air by weighing the mercury required.

Then if T = temperature to which the globe was heated,
t = temperature at which the globe was weighed *after* sealing,
V = capacity of globe,
v = volume of residual air at temperature t,
P = difference between the two weighings,
H = height of barometer (corrected).

$$D = \frac{P + (V - v)\frac{0{\cdot}0012932}{760\,(1 + 0{\cdot}00367t)}H}{\frac{0{\cdot}0012932}{760\,(1 + 0{\cdot}00367\,T)}\left[V\left(1 + k\,(T - t)\right) - v\frac{1 + 0{\cdot}00367\,T}{1 + 0{\cdot}00367t}\right]H}$$

then if $\frac{1 + 0{\cdot}00367\,T}{1 + 0{\cdot}00367t}$ we write γ

$$D = \frac{P + (V - v)\,a\,H}{a\,(V\beta - v\,\gamma)\,H}$$

* Phil. Trans., 1857, 460. † Comptes Rendus, 56, 891.

Before proceeding with the consideration of the logarithmic formula, I wish to notice the reasons given in Gerhardt and Ganot for a part of the formula. I find in both these works the statement that the weight of the globe = weight of globe filled with air − weight of air contained in globe. Now, seeing that the globe is weighed in air, and with the point open, the air in the globe must be exactly counterbalanced by the surrounding atmosphere; the weight found will then be the weight of the globe, − the weight of the air displaced by the substance of the globe; this last quantity may be disregarded, as the variations in its value for any small changes of temperature will be inappreciable. The weight of the vapour will then be P + the weight of the volume $(V - v)$ of air which it displaces.

In Gerhardt we find the following expression for a Dumas' vapour-density :—

$$D = A + B$$

$$\log. A = \log. V + \log. (1 + 0{\cdot}00367\,T) - \log. (V - v) - \log. \big(1 + k\,(T - t)\big) - \log. (1 + 0{\cdot}00367t)$$

$$\log. B = \log. A + \log. P - \log. \Big(\frac{0{\cdot}0012932}{760\,(1 + 0{\cdot}00367t)} H\Big) - \log. V$$

This logarithmic expression, when reduced to a formula, becomes—

$$D = \frac{P + V\frac{0{\cdot}0012932}{760\,(1 + 0{\cdot}00367t)} H}{\big(V - v\big)\big(1 + k\,(T - t)\big)\frac{0{\cdot}0012932}{760\,(1 + 0{\cdot}00367\,T)} H}$$

on examining which, it will be found that the residual air is ignored in the numerator, and in the denominator there is no correction made for its expansion; but if we modify the complete formula very slightly, we obtain the following expression :—

$$D = \frac{P + (V - v)\frac{0{\cdot}0012932}{760\,(1 + 0{\cdot}00367t)} H}{\Big(V - v\frac{1 + 0{\cdot}00367\,T}{1 + 0{\cdot}00367t}\Big)\big(1 + k\,(T - t)\big)\frac{0{\cdot}0012932}{760\,(1 + 0{\cdot}00367\,T)} H}$$

which is correct in the numerator, and in the denominator only introduces the small error of $v\,\dfrac{1 + 0{\cdot}00367\,T}{1 + 0{\cdot}00367t}\,k\,(T - t)$ which is inappreciable, unless the volume of the residual air be large and a high temperature be employed in the experiment.

In order to avail ourselves of logarithms we must use the form $D = A + B$.

$$\text{then } \log. A = \log. P - \log.\left(V - v\frac{1 + 0{\cdot}00367\,T}{1 + 0{\cdot}00367t}\right) - \log.\left(1 + k\,(T - t)\right) - \log.\left(\frac{0{\cdot}0012932}{760(1 + 0{\cdot}00367\,T)}H\right)$$

$$\text{and } \log. B = \log.\left(\frac{0{\cdot}0012932}{760\,(1 + 0{\cdot}00367t)}H\right) + \log.\,(V - v) + \log. A - \log. P.$$

$$\text{and } \log. A = \log. P - \log.\,(V - v\,\gamma) - \log.\,\beta - \log.\,\alpha - \log. H$$

$$\text{and } \log. B = \log.\,(\alpha H) + \log.\,(V - v) + \log. A - \log. P$$

Regnault's* modification consists in heating the substance in the globe under diminished pressure, and therefore at a much lower temperature than is possible by the ordinary method. The pressure (H) must be ascertained by means of a manometer connected with the apparatus. The details and formula are the same as in the original method, except that the neck of the globe is made very narrow at one point to admit of its being sealed off while still connected with the manometer.

For determinations at temperatures above that at which a mercurial thermometer can be conveniently used, *i.e.*, above 300°, it is proposed by Deville and Troost† to heat the globes in the vapours of substances which have high and known boiling-points. The apparatus employed by them for this purpose is applicable at any temperature up to 1040°; but, for temperatures up to 440°, the highest point at which glass globes can be used without fear of softening, the simpler apparatus proposed by Greville Williams‡ is all that is required. For a temperature of 350° the globe is heated in the vapour of boiling mercury, and for a temperature of 440° boiling sulphur is employed. For higher temperatures the more elaborate apparatus of Deville and Troost must be employed with porcelain globes. A temperature of 860° is obtained by heating the globe in the vapour of boiling cadmium, and by replacing the cadmium by zinc we obtain a temperature of 1040°. In these cases the details and formulæ are the same as in the ordinary Dumas' method; the following data will facilitate the calculation :—

* Regnault, Cours Elementaire de Chimie, 4, 71.

† Ann. Chim. Phys., 3rd Series, 58, 257.

‡ Watts' Dict. Chem., 5, 374.

T	a	$\log a$	β	$\log \beta$
350	0·00000074483	$\bar{7}$·8720609	1·0109	0·0047082
440	65074	8134136	1·0131	56523
860	40940	6121557	1·0091*	39213
1040	35325	5480935	1·0110	47555

A very useful modification of Dumas' method has been proposed by Grabowski†, as, although it necessitates the employment of a thermometer of some description, it is not necessary that it be correctly graduated, as the only thing requisite is that the oil-bath be heated to the same temperature (whatever it may be) during both parts of the operation, which is conducted as follows :—A glass globe is weighed full of dry air at the atmospheric temperature and pressure; it is then heated in an oil-bath, and the position of the mercury in the thermometer is registered; it is then sealed, cooled, and weighed. The point is then cut off, and the globe is weighed again, in order to determine the weight of glass lost in opening the point. The substance is then introduced and the globe is heated to the same temperature as before, and is then sealed, cooled, and weighed. Then if the atmospheric temperature (t) and pressure (H) have been the same throughout,

and if V = volume of globe,
and P = weight of globe at first weighing,
P' = „ second „
P'' = „ third „
P''' = „ fourth „

$$D = \frac{P''' - P'' + V\,\frac{0{\cdot}0012932}{760\,(1 + 0{\cdot}00367t)}H}{P' - P + V\,\frac{0{\cdot}0012932}{760\,(1 + 0{\cdot}00367t)}H}$$

$$= \frac{P''' - P'' + V\,a\,H}{P' - P + V\,a\,H}$$

The following method, proposed by Deville and Troost,‡ renders the calculation of the result as simple as in the preceding case, but has the advantage of not requiring any thermometer. By the side of the globe in which the substance is being heated a globe, of as nearly as possible the same size, containing air or iodine is placed; the two globes are then

* The mean co-efficient of expansion of porcelain is 0·0000108.
† Loc. cit. ‡ Comptes Rendus, 56, 891.

sealed at the same time, cooled and weighed (at temperature t and pressure H); then if

P = weight of the globe in which the substance is to be heated,
P' = weight after sealing of globe containing substance,
P'' = weight of globe to be used for air or iodine,
P''' = weight after sealing of globe containing air or iodine,
V = volume of globe containing substance,
V' = volume of globe containing air or iodine;

and if air be used as the standard,

$$D = \frac{\left(P' - P + V\frac{0{\cdot}0012932}{760\,(1+0{\cdot}00367t)}H\right)V'}{\left(P''' - P'' + V'\frac{0{\cdot}0012932}{760\,(1+0{\cdot}00367t)}H\right)V} = \frac{(P' - P + V\,a\,H)V'}{(P''' - P'' + V'a\,H)V}$$

and in the case of iodine being used—

$$D = 8{\cdot}716\ \frac{(P' - P + V\,a\,H)V'}{(P' - P'' + V'a\,H)V}.$$

This formula cannot be used if there is much residual air in either of the globes; in that case it is necessary to determine T with the ordinary Dumas' formula by means of the iodine globe, substituting for D its value 8·716. After determining T, the vapour-density of the substance is found by means of the complete Dumas' formula already given. In this method mercury cannot be substituted for iodine, as it condenses in the neck of the globe, and the cold drops fall back into the hot globe, and in so doing are very liable to break it.

Regnault's* method for accomplishing the same object is available only where the boiling-point of the substance is high, and a large quantity can be obtained for the experiment, as there is no means of determining the residual air. The apparatus consists of two iron bottles, of nearly the same capacity, whose necks are partially closed by imperfectly-fitting stoppers; in one of these the substance is heated in a muffle, and in the other, which is heated at the same time, some mercury is placed before heating. They are then withdrawn and allowed to cool and the amounts left in the two flasks are determined by dissolving out the substances and estimating the quantities by appropriate means.

* Ann. Chim. Phys. 3rd Series, 63, 45.

Then if P = weight of mercury found,
P' = weight of substance found,
V = volume of flask in which mercury was heated,
V' = volume of flask in which substance was heated,

$$D = 6{\cdot}9 \frac{P'}{P} \frac{V}{V'}$$

In Regnault's* method, in which the air-thermometer is employed, it is not necessary to know the temperature at the time of sealing, as the weight of the vapour is compared with the weight of the volume of air which has been heated at the same time. With reference to the globe containing the substance, the following letters, viz., P, H, V, and t, have the same meanings as in the Dumas' formula.

Then if W' = weight of mercury which completely fills the air-thermometer at 0°,
W = weight of mercury which has entered the air-thermometer after it has been cooled down to 0°, and the point has been opened,
h = height of mercury in air-thermometer above the level of the cistern,

$$D = \frac{P + V\frac{0{\cdot}0012932}{760\,(1 + 0{\cdot}00367t)}H}{\frac{W' - W}{W'} V \frac{0{\cdot}0012932}{760}(H - h)}$$

$$= \frac{P + V a H}{\frac{W' - W}{W'} V a (H - h)}$$

Playfair and Wanklyn's† method, which has the advantage of being applicable in the case of liquids which decompose on being heated, is so complicated in its details that a condensed formula is impossible; we must therefore refer the reader to the original paper.

* Regnault, Cours Elementaire de Chimie, 4, 63.
† Trans. Roy. Soc. Edin., *loc. cit.*

$$\frac{0{\cdot}0012932}{760\ (1+0{\cdot}00367\ t)} = a$$

t.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	0·00000170157	0095	0033	*9970	9908	9846	9784	9721	9659	9597
1	169535	9473	9411	9349	9288	9226	9164	9102	9041	8979
2	8918	8856	8795	8733	8672	8610	8549	8488	8427	8365
3	8304	8243	8182	8121	8060	7999	7939	7878	7817	7756
4	7696	7635	7574	7514	7453	7393	7332	7272	7212	7152
5	7091	7031	6971	6911	6851	6791	6731	6671	6611	6551
6	6491	6431	6372	6312	6252	6193	6133	6074	6014	5955
7	5896	5836	5777	5718	5658	5599	5540	5481	5422	5363
8	5304	5245	5186	5127	5069	5010	4951	4893	4834	4775
9	4717	4658	4600	4541	4483	4425	4366	4308	4250	4192
10	4134	4076	4018	3960	3902	3844	3786	3728	3670	3612
11	3555	3497	3439	3382	3324	3267	3209	3152	3094	3037
12	2980	2922	2865	2808	2751	2694	2637	2580	2523	2466
13	2409	2352	2295	2238	2182	2125	2068	2012	1955	1898
14	1842	1785	1729	1673	1616	1560	1504	1447	1391	1335
15	1279	1223	1167	1111	1055	0999	0943	0887	0831	0776
16	0720	0664	0609	0553	0497	0442	0386	0331	0275	0220
17	0165	0109	0054	*9999	9944	9889	9833	9778	9723	9668
18	159613	9558	9503	9449	9394	9339	9284	9230	9175	9120
19	9066	9011	8957	8902	8848	8793	8739	8685	8630	8576
20	8522	8468	8414	8359	8305	8251	8197	8143	8089	8036
21	7982	7928	7874	7820	7767	7713	7659	7606	7552	7499
22	7445	7392	7338	7285	7232	7178	7125	7072	7019	6966
23	6912	6859	6806	6753	6700	6647	6594	6542	6489	6436
24	6383	6330	6278	6225	6172	6120	6067	6015	5962	5910
25	5857	5805	5753	5700	5648	5596	5544	5492	5439	5387
26	5335	5283	5231	5179	5127	5075	5024	4972	4920	4868
27	4817	4765	4713	4662	4610	4559	4507	4456	4404	4353
28	4301	4250	4199	4147	4096	4045	3994	3943	3892	3841
29	3790	3739	3688	3637	3586	3535	3484	3433	3383	3332

$$\text{Log.}\frac{0\ 0012932}{760\ (1\ +\ 0{\cdot}00367\ t.)} = \log.\ a.$$

t.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	$\bar{6}$ 230852	0692	0533	0374	0215	0056	*9896	9737	9579	9420
1	229261	9102	8943	8785	8626	8467	8309	8151	7992	7834
2	7676	7517	7359	7201	7043	6885	6727	6569	6412	6254
3	6096	5939	5781	5624	5466	5309	5151	4994	4837	4680
4	4523	4366	4209	4052	3895	3738	3581	3424	3268	3111
5	2955	2798	2642	2485	2329	2173	2017	1860	1704	1548
6	1392	1236	1080	0925	0769	0613	0458	0302	0146	*9991
7	219835	9680	9525	9370	9214	9059	8904	8749	8594	8439
8	8284	8130	7975	7820	7666	7511	7356	7202	7047	6893
9	6739	6584	6430	6276	6122	5968	5814	5660	5506	5352
10	5199	5045	4891	4738	4584	4431	4277	4124	3970	3817
11	3664	3511	3358	3204	3051	2898	2746	2593	2440	2287
12	2135	1982	1829	1677	1524	1372	1220	1067	0915	0763
13	0611	0458	0306	0154	0002	*9851	9699	9547	9395	9244

$$\text{Log.}\ \frac{0\cdot0012932}{760\ (1 + 0\cdot00367\ t)} = \log.\ a.$$

t.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
14	$\bar{6}$.209092	8940	8789	8637	8486	8335	8183	8032	7881	7730
15	7579	7428	7277	7126	6975	6824	6673	6522	6372	6221
16	6071	5920	5770	5619	5469	5318	5168	5018	4868	4718
17	4568	4418	4268	4118	3968	3818	3668	3519	3369	3220
18	3070	2921	2771	2622	2472	2323	2174	2025	1876	1726
19	1577	1428	1280	1131	0982	0833	0684	0536	0387	0239
20	0090	*9942	9793	9645	9496	9348	9200	9052	8904	8756
21	198608	8460	8312	8164	8016	7868	7721	7573	7425	7278
22	7130	6983	6836	6688	6541	6394	6246	6099	5952	5805
23	5658	5511	5364	5217	5071	4924	4777	4631	4484	4337
24	4191	4044	3898	3752	3605	3459	3313	3167	3021	2875
25	2728	2583	2437	2291	2145	1999	1853	1708	1562	1417
26	1271	1126	0980	0835	0689	0544	0399	0254	0109	*9963
27	189818	9673	9529	9384	9239	9094	8949	8804	8660	8515
28	8371	8226	8082	7937	7793	7649	7504	7360	7216	7072
29	6928	6784	6640	6496	6352	6208	6064	5921	5777	5633

$$\text{Log.}\ \frac{0\cdot0012932}{760\ (1 + 0\cdot00367\ T)} = \log.\ \alpha.$$

T.	Log. α.	Diff.	T.	Log. α.	Diff.	T.	Log. α.	Diff.
30	$\bar{6}$·185490	718	44·5	$\bar{6}$·165154	684	68	$\bar{6}$·134095	1274
30·5	184772	716	45	164470	684	69	132821	1270
31	184056	715	45·5	163786	682	70	131551	1266
31·5	183341	714	46	163104	681	71	130285	1263
32	182627	712	46·5	162423	681	72	129022	1259
32·5	181915	712	47	161742	679	73	127763	1255
33	181203	710	47·5	161063	678	74	126508	1252
33·5	180493	709	48	160385	677	75	125256	1248
34	179784	708	48·5	159708	676	76	124008	1244
34·5	179076	707	49	159032	675	77	122764	1241
35	178369	705	49·5	158357	674	78	121523	1237
35·5	177664	705	50	157683	1344	79	120286	1234
36	176959	703	51	156339	1341	80	119052	1231
36·5	176256	702	52	154998	1336	81	117821	1227
37	175554	701	53	153662	1332	82	116594	1223
37·5	174853	700	54	152330	1329	83	115371	1220
38	174153	699	55	151001	1324	84	114151	1217
38·5	173454	698	56	149677	1320	85	112934	1213
39	172756	697	57	148357	1316	86	111721	1210
39·5	172059	695	58	147041	1312	87	110511	1206
40	171364	694	59	145729	1308	88	109305	1203
40·5	170670	694	60	144421	1305	89	108102	1200
41	169976	692	61	143116	1300	90	106902	1196
41·5	169284	691	62	141816	1296	91	105706	1194
42	168593	690	63	140520	1293	92	104512	1189
42·5	167903	689	64	139227	1289	93	103323	1187
43	167214	687	65	137938	1285	94	102136	1184
43·5	166527	687	66	136653	1281	95	100952	1180
44	165840	686	67	135372	1277	96	099772	1177

$$\text{Log.}\ \frac{0\cdot0012932}{760\ (1\ +\ 0\cdot00367\ T)} = \log.\ \alpha.$$

T.	Log. α.	Diff.	T.	Log. α.	Diff	T.	Log. α.	Diff.
97	$\bar{6}\cdot098595$	1174	151	$\bar{6}\cdot039353$	1024	205	$\bar{7}\cdot987231$	909
98	097421	1170	152	038329	1022	206	986322	906
99	096251	1168	153	037307	1020	207	985416	905
100	095083	1164	154	036287	1017	208	984511	903
101	093919	1161	155	035270	1015	209	983608	901
102	092758	1159	156	034255	1012	210	982707	900
103	091599	1155	157	033243	1010	211	981807	897
104	090444	1152	158	032233	1008	212	980910	895
105	089292	1149	159	031225	1005	213	980015	894
106	088143	1146	160	030220	1003	214	979121	892
107	086997	1143	161	029217	1001	215	978229	890
108	085854	1140	162	028216	998	216	977339	888
109	084714	1137	163	027218	996	217	976451	886
110	083577	1134	164	026222	994	218	975565	885
111	082443	1131	165	025228	992	219	974680	883
112	081312	1128	166	024236	989	220	973797	881
113	080184	1125	167	023247	987	221	972916	879
114	079059	1122	168	022260	985	222	972037	877
115	077937	1120	169	021275	983	223	971160	876
116	076817	1116	170	020292	980	224	970284	874
117	075701	1114	171	019312	978	225	969410	872
118	074587	1111	172	018334	976	226	968538	870
119	073476	1107	173	017358	974	227	967668	869
120	072369	1106	174	016384	972	228	966799	867
121	071263	1102	175	015412	269	229	965932	865
122	070161	1099	176	014443	267	230	965067	863
123	069062	1097	177	013476	966	231	964204	862
124	067965	1094	178	012510	963	232	963342	860
125	066871	1091	179	011547	960	233	962482	858
126	065780	1089	180	010587	959	234	961624	857
127	064691	1086	181	009628	957	235	960767	855
128	063605	1083	182	008671	954	236	959912	853
129	062522	1080	183	007717	953	237	959059	852
130	061442	1078	184	006764	950	238	958207	850
131	060364	1075	185	005814	948	239	957357	848
132	059289	1072	186	004866	947	240	956509	847
133	058217	1070	187	003919	944	241	955662	845
134	057147	1067	188	002975	942	242	954817	843
135	056080	1065	189	002033	940	243	953974	842
136	055015	1062	190	001093	938	244	953132	840
137	053953	1059	191	000155	936	245	952292	838
138	052894	1057	192	$\bar{7}\cdot999219$	934	246	951454	837
139	051837	1054	193	998285	932	247	950617	835
140	050783	1051	194	997353	930	248	949782	834
141	049732	1050	195	996423	928	249	948948	832
142	048682	1046	196	995495	926	250	948116	830
143	047636	1044	197	994569	924	251	947286	829
144	046592	1042	198	993645	922	252	946457	827
145	045550	1039	199	992723	920	253	945630	826
146	044511	1036	200	991803	919	254	944804	824
147	043475	1034	201	990884	916	255	943980	823
148	042441	1032	202	989968	914	256	943157	821
149	041409	1029	203	989054	913	257	942336	819
150	040380	1027	204	988141	910	258	941517	818

$$\text{Log.}\ \frac{0{\cdot}0012932}{760\,(1+0{\cdot}00367\,T)} = \log.\ \alpha.$$

T.	Log. α	Diff.	T.	Log. α.	Diff.	T.	Log. α.	Diff.
259	$\bar{7}$·940699	816	273	$\bar{7}$·929407	795	287	$\bar{7}$·918401	775
260	939883	815	274	928612	794	288	917626	774
261	939068	814	275	927818	793	289	916852	773
262	938254	811	276	927025	791	290	916079	772
263	937443	811	277	926234	790	291	915307	770
264	936632	808	278	925444	788	292	914537	768
265	935824	808	279	924656	787	293	913769	768
266	935016	805	280	923869	785	294	913001	766
267	934211	805	281	923084	784	295	912235	764
268	933406	802	282	922300	782	296	911471	764
269	932604	802	283	921518	782	297	910707	762
270	931802	800	284	920736	779	298	909945	760
271	931002	798	285	919957	779	299	909185	759
272	930204	797	286	919178	777	300	908426	

$$\frac{0{\cdot}0012932}{760\,(1+0{\cdot}00367t)}\,H = \alpha\,H$$

H	735	736	737	738	739	740	741	742	743	744	745	746	747	748	749	750	751	752	H
t																			t
10	0·0012063	080	096	113	129	145	162	178	195	211	227	244	260	277	293	310	326	342	10
10·5	042	058	075	091	108	124	140	157	173	190	206	222	239	255	271	288	304	321	10·5
11	021	037	054	070	086	103	119	135	152	168	184	201	217	233	250	266	282	299	11
11·5	000	016	032	049	065	081	098	114	130	147	163	179	196	212	228	245	261	277	11·5
12	0·0011979	995	*011	027	044	060	076	093	109	125	142	158	174	190	207	223	239	256	12
12·5	958	974	990	*006	023	039	055	071	088	104	120	136	153	169	185	202	218	234	12·5
13	937	953	969	985	*002	018	034	050	067	083	099	115	131	148	164	180	196	213	13
13·5	916	932	948	964	981	997	*013	029	045	062	078	094	110	126	143	159	175	191	13·5
14	895	911	927	943	960	976	992	*008	024	041	057	073	089	105	121	138	154	170	14
14·5	874	890	907	923	939	955	971	987	*003	020	036	052	068	084	100	117	133	149	14·5
15	854	870	886	902	918	934	950	966	983	999	*015	031	047	063	079	095	112	128	15
15·5	833	849	865	881	897	913	930	946	962	978	994	*010	026	042	058	074	091	107	15·5
16	812	829	845	861	877	893	909	925	941	957	973	989	*005	021	037	054	070	086	16
16·5	792	808	824	840	856	872	888	904	920	936	952	968	985	*001	017	033	049	065	16·5
17	772	788	804	820	836	852	868	884	900	916	932	948	964	980	996	*012	028	044	17
17·5	751	767	783	799	815	831	847	863	879	895	911	927	943	959	975	991	*007	023	17·5
18	731	747	763	779	795	811	827	843	859	875	891	907	923	939	955	971	986	*002	18
18·5	711	727	743	759	775	791	807	822	838	854	870	886	902	918	934	950	966	982	18·5
19	691	707	723	739	754	770	786	802	818	834	850	866	882	898	914	929	945	961	19
19.5	671	687	703	718	734	750	766	782	798	814	830	846	861	877	893	909	925	941	19·5
20	651	667	683	698	714	730	746	762	778	794	809	825	841	857	873	889	905	920	20
20·5	631	647	663	678	694	710	726	742	758	773	789	805	821	837	853	868	884	900	20·5
21	611	627	643	659	674	690	706	722	738	753	769	785	801	817	832	848	864	880	21
21·5	591	607	623	639	655	670	686	702	718	733	749	765	781	796	812	828	844	860	21·5
22	572	588	603	619	635	650	666	682	698	713	729	745	761	776	792	808	824	839	22
22·5	552	568	584	599	615	631	646	662	678	694	709	725	741	756	772	788	804	819	22·5
23	533	548	564	580	595	611	627	642	658	674	690	705	721	737	752	768	784	799	23
23·5	513	529	544	560	576	591	607	623	638	654	670	685	701	717	732	748	764	779	23·5
24	494	509	525	541	556	572	588	603	619	634	650	666	681	697	713	728	744	760	24
24·5	474	490	506	521	537	552	568	584	599	615	630	646	662	677	693	709	724	740	24·5
25	455	471	486	502	517	533	549	564	580	595	611	627	642	658	673	689	704	720	25

$$H\frac{0{\cdot}0012932}{760\ (1+0{\cdot}00367t)}=\alpha H$$

H	753	754	755	756	757	758	759	760	761	762	763	764	765	766	767	768	769	770	H
t																			t
10	0·0012359	375	392	408	424	441	457	474	490	507	523	539	556	572	589	605	621	638	10
10·5	337	353	370	386	403	419	435	452	468	484	501	517	534	550	566	583	599	616	10·5
11	315	332	348	364	381	397	413	430	446	462	479	495	511	528	544	561	577	593	11
11·5	294	310	326	343	359	375	391	408	424	440	457	473	489	506	522	538	555	571	11·5
12	272	288	305	321	337	353	370	386	402	419	435	451	467	484	500	516	533	549	12
12·5	250	267	283	299	315	332	348	364	381	397	413	429	446	462	478	494	511	527	12·5
13	229	245	261	278	294	310	326	343	359	375	391	408	424	440	456	473	489	505	13
13·5	208	224	240	256	272	289	305	321	337	353	370	386	402	418	435	451	467	483	13·5
14	186	202	219	235	251	267	283	300	316	332	348	364	380	397	413	429	445	461	14
14·5	165	181	197	213	230	246	262	278	294	310	327	343	359	375	391	407	423	440	14·5
15	144	160	176	192	208	224	241	257	273	289	305	321	337	354	370	386	402	418	15
15·5	123	139	155	171	187	203	219	235	252	268	284	300	316	332	348	364	380	396	15·5
16	102	118	134	150	166	182	198	214	230	246	262	279	295	311	327	343	359	375	16
16·5	081	097	113	129	145	161	177	193	209	225	241	257	273	289	305	321	338	354	16·5
17	060	076	092	108	124	140	156	172	188	204	220	236	252	268	284	300	316	332	17
17·5	039	055	071	087	103	119	135	151	167	183	199	215	231	247	263	279	295	311	17·5
18	018	034	050	066	082	098	114	130	146	162	178	194	210	226	242	258	274	290	18
18·5	0·0011998	*014	030	046	062	077	093	109	125	141	157	173	189	205	221	237	253	269	18·5
19	977	993	*009	025	041	057	073	089	104	120	136	152	168	184	200	216	232	248	19
19·5	957	973	988	*004	020	036	052	068	084	100	115	131	147	163	179	195	211	227	19·5
20	936	952	968	984	*000	015	031	047	063	079	095	111	126	142	158	174	190	206	20
20·5	916	932	948	963	979	995	*011	027	042	058	074	090	106	122	137	153	169	185	20·5
21	896	911	927	943	959	975	990	*006	022	038	054	069	085	101	117	133	148	164	21
21·5	875	891	907	923	938	954	970	986	*001	017	033	049	065	080	096	112	128	143	21·5
22	855	871	887	902	918	934	950	965	981	997	*013	028	044	060	076	091	107	123	22
22·5	835	851	867	882	898	914	929	945	961	977	992	*008	024	039	055	071	087	102	22·5
23	815	831	846	862	878	893	909	925	941	956	972	988	*003	019	035	050	066	082	23
23·5	795	811	826	842	858	873	889	905	920	936	952	967	983	999	*014	030	046	061	23·5
24	775	791	806	822	838	853	869	885	900	916	932	947	963	978	994	*010	025	041	24
24·5	755	771	787	802	818	833	849	865	880	896	911	927	943	958	974	990	*005	021	24·5
25	736	751	767	782	798	814	829	845	860	876	891	907	923	938	954	969	985	*001	25

$$\text{Log.}\left(H\,\frac{0{\cdot}0012932}{760\,(1+0{\cdot}00367t)}\right)=\text{Log. }\alpha\,H.$$

H	735	736	737	738	739	740	741	742	743	744	745	746	747	748	749	750	751	752	H
Log. H	2·866287	6877	7467	8056	8644	9231	9818	*0403	0988	1572	2156	2738	3320	3901	4481	5061	5639	6217	Log. H
t																			t
10	$\bar{3}$·081486	2076	2666	3255	3843	4430	5017	5602	6187	6771	7355	7937	8519	9100	9680	*0260	0838	1416	10
10·5	0718	1308	1898	2487	3075	3662	4249	4834	5419	6003	6587	7169	7751	8332	8912	9492	*0070	0648	10·5
11	079951	*0542	1131	1720	2308	2896	3482	4068	4653	5327	5820	6403	6984	7565	8146	8725	9304	9882	11
11·5	9186	9776	*0366	0955	1543	2130	2717	3302	3887	4471	5055	5637	6219	6800	7380	7960	8538	9116	11·5
12	8422	9012	9602	*0191	0779	1366	1953	2538	3123	3707	4291	4873	5455	6036	6616	7196	7774	8352	12
12·5	7659	8250	8839	9428	*0016	0604	1190	1776	2361	2945	3528	4111	4692	5273	5854	6433	7012	7590	12·5
13	6898	7488	8078	8667	9255	9842	*0429	1014	1599	2183	2767	3349	3931	4512	5092	5672	6250	6828	13
13·5	6138	6728	7318	7907	8495	9082	9669	*0255	0839	1424	2007	2589	3171	3752	4332	4912	5491	6068	13·5
14	5379	5970	6559	7148	7736	8324	8910	9496	*0081	0665	1248	1831	2413	2994	3574	4153	4732	5310	14
14·5	4622	5212	5802	6391	6979	7566	8153	8738	9323	9907	*0491	1073	1655	2236	2816	3396	3974	4552	14·5
15	3866	4456	5046	5635	6223	6810	7397	7982	8567	9151	9735	*0317	0899	1480	2060	2640	3218	3796	15
15·5	3111	3702	4291	4880	5468	6056	6642	7228	7813	8397	8980	9563	*0145	0726	1306	1885	2464	3042	15·5
16	2358	2948	3538	4127	4715	5302	5889	6474	7059	7643	8227	8809	9391	9972	*0552	1132	1710	2288	16
16·5	1606	2196	2786	3375	3963	4550	5137	5722	6307	6891	7475	8057	8639	9220	9800	*0380	0958	1536	16·5
17	0855	1445	2035	2624	3212	3799	4386	4972	5556	6141	6724	7306	7888	8469	9049	9629	*0208	0785	17
17·5	0105	0696	1286	1875	2463	3050	3636	4222	4807	5391	5974	6557	7139	7720	8300	8879	9458	*0036	17·5
18	069357	9948	*0538	1126	1714	2302	2888	3474	4059	4643	5226	5809	6391	6972	7552	8131	8710	9288	18
18·5	8610	9201	9791	*0379	0967	1555	2141	2727	3312	3896	4479	5062	5644	6225	6805	7384	7963	8541	18·5
19	7865	8455	9045	9634	*0222	0809	1396	1981	2566	3150	3734	4316	4898	5479	6059	6639	7217	7795	19
19·5	7120	7711	8301	8890	9478	*0065	0651	1237	1822	2406	2989	3572	4154	4735	5315	5894	6473	7051	19·5
20	6377	6968	7558	8146	8734	9322	9908	*0494	1079	1663	2246	2829	3411	3992	4572	5151	5730	6308	20
20·5	5636	6226	6816	7405	7993	8580	9166	9752	*0337	0921	1505	2087	2669	3250	3830	4410	4988	5566	20·5
21	4895	5486	6075	6664	7252	7839	8426	9012	9597	*0181	0764	1347	1928	2509	3090	3669	4248	4826	21
21·5	4156	4746	5336	5925	6513	7100	7687	8272	8857	9441	*0025	0607	1189	1770	2350	2930	3508	4086	21·5
22	3418	4008	4598	5187	5775	6362	6949	7534	8119	8703	9287	9869	*0451	1032	1612	2192	2770	3348	22
22·5	2681	3271	3861	4450	5038	5625	6212	6798	7382	7967	8550	9132	9714	*0295	0875	1455	2034	2611	22·5
23	1945	2536	3126	3715	4303	4890	5476	6062	6647	7231	7814	8397	8979	9560	*0140	0719	1298	1876	23
23·5	1211	1802	2391	2980	3568	4156	4742	5328	5913	6497	7080	7663	8244	8825	9406	9985	*0564	1142	23·5
24	0478	1069	1658	2247	2835	3423	4009	4595	5180	5764	6347	6930	7511	8092	8673	9252	9831	*0409	24
24·5	059746	0337	0927	1515	2103	2691	3277	3863	4448	5032	5615	6198	6780	7361	7941	8520	9099	9677	24·5
25	9016	9606	*0196	0785	1373	1960	2547	3132	3717	4301	4885	5467	6049	6630	7210	7790	8368	8946	25

$$\text{Log.}\left(H\,\frac{0{\cdot}0012932}{760(1+0{\cdot}00367t)}\right) = \text{Log.}\,\alpha\,H.$$

H	753	754	755	756	757	758	759	760	761	762	763	764	765	766	767	768	769	770	H
Log. H	$\bar{2}\cdot876795$	7371	7947	8521	9095	9669	*0241	0813	1384	1955	2524	3093	3661	4228	4795	5361	5926	6490	Log. H
t																			t
10	$\bar{3}\cdot091994$	2570	3146	3720	4294	4868	5440	6012	6583	7154	7723	8292	8860	9427	9994	*0560	1125	1689	10
10·5	1226	1802	2378	2952	3526	4100	4672	5244	5815	6386	6955	7524	8092	8659	9226	9792	*0357	0921	10·5
11	0459	1035	1611	2186	2760	3333	3906	4477	5049	5619	6188	6757	7325	7893	8459	9025	9590	*0155	11
11·5	·089693	*0270	0845	1420	1994	2568	3140	3712	4283	4853	5422	5992	6560	7127	7694	8260	8825	9389	11·5
12	8930	9506	*0082	0656	1230	1804	2376	2948	3519	4090	4659	5228	5796	6363	6930	7496	8061	8625	12
12·5	8167	8743	9319	9894	*0468	1041	1614	2185	2757	3327	3896	4465	5033	5601	6167	6733	7298	7863	12·5
13	7406	7982	8558	9132	9706	*0280	0852	1424	1995	2566	3135	3704	4272	4839	5406	5972	6537	7101	13
13·5	6646	7222	7798	8372	8947	9520	*0092	0664	1235	1806	2375	2944	3512	4079	4646	5212	5777	6341	13·5
14	5887	6463	7039	7614	8188	8761	9334	9906	*0477	1047	1616	2185	2753	3321	3887	4453	5018	5583	14
14·5	5130	5706	6282	6856	7430	8004	8576	9148	9719	*0290	0859	1428	1996	2563	3130	3696	4261	4825	14·5
15	4374	4950	5526	6100	6674	7248	7820	8392	8963	9534	*0103	0672	1240	1807	2374	2940	3505	4069	15
15·5	3619	4195	4771	5346	5920	6493	7066	7638	8209	8779	9348	9917	*0485	1053	1619	2185	2750	3315	15·5
16	2866	3442	4018	4592	5166	5740	6312	6884	7455	8026	8595	9164	9732	*0299	0866	1432	1997	2561	16
16·5	2113	2690	3265	3840	4414	4988	5560	6132	6703	7273	7843	8412	8980	9547	*0114	0680	1245	1809	16·5
17	1363	1939	2515	3089	3664	4237	4809	5381	5952	6523	7092	7661	8229	8796	9363	9929	*0494	1058	17
17·5	0613	1189	1765	2340	2914	3487	4060	4632	5203	5773	6343	6912	7480	8047	8614	9179	9744	*0309	17·5
18	·079865	*0441	1017	1592	2166	2739	3312	3884	4455	5025	5595	6163	6731	7299	7865	8431	8996	9561	18
18·5	9118	9694	*0270	0845	1419	1992	2565	3137	3708	4278	4848	5416	5984	6552	7118	7684	8249	8814	18·5
19	8372	8949	9524	*0099	0673	1247	1819	2391	2962	3532	4102	4671	5239	5806	6373	6939	7504	8068	19
19·5	7628	8204	8780	9355	9929	*0502	1075	1647	2218	2788	3358	3927	4495	5062	5629	6194	6759	7324	19·5
20	6885	7461	8037	8612	9186	9759	*0332	0904	1475	2045	2615	3183	3751	4319	4885	5451	6016	6581	20
20·5	6143	6720	7295	7870	8444	9017	9590	*0162	0733	1303	1873	2442	3010	3577	4144	4709	5275	5839	20·5
21	5403	5979	6555	7130	7704	8277	8850	9421	9992	*0563	1132	1701	2269	2837	3403	3969	4534	5098	21
21·5	4663	5240	5815	6390	6964	7538	8110	8682	9253	9823	*0393	0962	1530	2097	2664	3230	3795	4359	21·5
22	3925	4502	5077	5652	6226	6800	7372	7944	8515	9085	9655	*0224	0792	1359	1926	2492	3057	3621	22
22·5	3189	3765	4341	4915	5490	6063	6635	7207	7778	8349	8918	9487	*0055	0622	1189	1755	2320	2884	22·5
23	2453	3029	3605	4180	4754	5327	5900	6472	7043	7613	8183	8752	9320	9887	*0454	1019	1584	2149	23
23·5	1719	2295	2871	3446	4020	4593	5166	5737	6309	6879	7448	8017	8585	9153	9719	*0285	0850	1415	23·5
24	0986	1562	2138	2713	3287	3860	4433	5004	5576	6146	6715	7284	7852	8420	8986	9552	*0117	0682	24
24·5	0254	0830	1406	1981	2555	3128	3701	4273	4844	5414	5984	6552	7120	7688	8254	8820	9385	9950	24·5
25	·069523	*0100	0675	1250	1824	2398	2970	3542	4113	4683	5253	5822	6390	6957	7524	8090	8655	9219	25

$$\log.\ (1 + k\,(T-t)) = \log.\ \beta.$$

$(T-t.)$	log. β.	$(T-t.)$	log. β.	$(T-t.)$	log. β.
35	0·000416	125	0·001539	215	0·002770
40	477	130	599	220	835
45	538	135	699	225	900
50	599	140	764	230	964
55	655	145	824	235	0·003111
60	716	150	889	240	176
65	776	155	954	245	240
70	837	160	0·002014	250	309
75	898	165	079	255	374
80	954	170	140	260	439
85	0·001045	175	205	265	503
90	106	180	265	270	572
95	166	185	386	275	637
100	231	190	451	280	701
105	292	195	516	285	856
110	353	200	580	290	921
115	413	205	641	295	990
120	474	210	706	300	0·004059

$$\frac{1 + 0{\cdot}00367\ \mathrm{T}}{1 + 0{\cdot}00367\ t} = \gamma.$$

	$t.$ 0	5	10	15	20	25	30
T.							
50	1·183	1·162	1·141	1·121	1·102	1·084	1·066
55	201	180	159	139	119	100	082
60	220	198	177	156	136	117	099
65	238	216	194	173	153	134	115
70	256	234	212	191	170	151	132
75	275	252	230	208	188	168	148
80	293	270	247	226	205	184	165
85	311	288	265	243	222	201	181
90	330	306	283	260	239	218	198
95	348	324	300	278	256	235	214
100	367	342	318	295	273	252	231
105	385	360	336	313	290	268	247
110	403	378	354	330	307	285	264
115	422	396	371	347	324	302	281
120	440	414	389	365	341	319	297
125	458	432	407	382	359	336	314
130	477	450	424	400	376	352	330
135	495	468	442	417	393	369	347
140	513	486	460	434	410	386	363
145	532	504	477	452	427	403	380
150	550	522	495	469	444	420	396
155	568	540	513	487	461	437	413
160	587	558	531	504	478	453	429
165	605	576	548	521	495	470	446
170	623	594	566	539	512	487	462
175	642	612	584	556	529	504	479

$$\frac{1 + 0{\cdot}00367\ T}{1 + 0{\cdot}00367\ t} = \gamma.$$

	t. 0	5	10	15	20	25	30
T.							
180	1·660	1·630	1·601	1·573	1·547	1·521	1·495
185	678	648	619	591	564	537	512
190	697	666	637	608	581	554	528
195	715	684	654	626	598	571	545
200	734	702	672	643	615	588	562
205	752	720	690	660	632	605	578
210	770	738	708	678	649	621	595
215	789	756	725	695	666	638	611
220	807	774	743	713	683	655	628
225	825	792	761	730	700	672	644
230	844	810	778	747	718	689	661
235	862	828	796	765	735	705	677
240	880	846	814	782	752	722	694
245	899	864	831	800	769	739	710
250	917	882	849	817	786	756	727
255	935	900	867	834	803	773	743
260	954	918	885	852	820	789	760
265	972	937	902	869	837	806	776
270	990	955	920	887	854	823	793
275	2·009	973	938	904	871	840	809
280	027	991	955	921	888	857	826
285	045	2·009	973	939	906	874	843
290	064	027	991	956	923	890	859
295	082	045	2·008	973	940	907	876
300	101	063	026	991	957	924	892
305	119	081	044	2·008	974	941	909
310	137	099	062	026	991	958	925
315	156	117	079	043	2·008	974	942
320	174	135	097	060	025	991	958
325	192	153	115	078	042	2·008	975
330	211	171	132	095	059	025	991
335	229	189	150	113	077	042	2·008
340	247	207	168	130	094	058	024
345	266	225	185	147	111	075	041
350	284	243	203	165	128	092	057

XXVI.—*Researches on Vanadium.* Part II.

By Henry E. Roscoe, B.A., Ph.D., F.R.S.

(Abstracted from the Philosophical Transactions for 1869.)

On the Chlorides of Vanadium and Metallic Vanadium.

In the first part of these researches* I stated that the nitride of vanadium forms the point from which the study of the vanadium compounds, properly so called, must be commenced. I now proceed to describe the composition and mode of preparation of the compounds of the metal with chlorine, and also the properties of the metal itself.

The process for preparing vanadium mononitride which I described in the last communication, was that proposed by Berzelius for obtaining the substance which he conceived to be metal. It consists in the action of dry ammoniacal gas upon vanadyl trichloride ($VOCl_3$).

Owing, however, to the difficulty of properly regulating the very violent action which occurs when the two bodies come into contact, and the consequent loss of trichloride, this method was unsuited for the preparation of the nitride in quantity. Seeking for an easier and more economical method, I found that if the black residue left on calcining ammonium metavanadate in the air (probably an oxynitride) be heated to whiteness for a sufficiently long time in a current of dry ammoniacal gas, pure vanadium mononitride, VN, is left behind.

This corresponds to 20·1 per cent. of nitrogen. A third and still more simple mode of obtaining the nitride is that of exposing the trioxide to the action of ammonia gas at a white heat. It is a remarkable fact, and one of which we know but two other examples, that in presence of nitrogen and hydrogen the whole oxygen of an oxide is displaced by nitrogen.

The Chlorides of Vanadium.

I have succeeded in preparing three chlorides of vanadium, viz. (1) vanadium tetrachloride, VCl_4; (2) vanadium trichloride, VCl_3; (3) vanadium dichloride, VCl_2.

* Bakerian Lecture, Philosophical Transactions, 1868, p. 1; Chem. Soc. J. [2], vi, 322.

(1). *Vanadium Tetrachloride*, VCl_4, molecular weight = 193·3, vapour-density = 96·6 (H = 1).—This chloride is formed as a dark reddish-brown volatile liquid when metallic vanadium or the mononitride is burnt in excess of chlorine.

Method 1.—The first method adopted for the preparation of the tetachloride was by passing dry chlorine gas over the mononitride heated to redness; the whole of the nitride volatilizes, and a reddish-brown liquid is obtained. In one operation 16·96 grms. of the mononitride yielded, on treatment with excess of chlorine, 44·3 grms. of the crude tetrachloride, the theoretical yield being 50·1 grms. Owing to the inevitable presence of traces of oxide in the nitride, the first few drops of the distillate consisted of the more volatile light-yellow oxytrichloride, and this portion was collected separately, before much of the dark tetrachloride had come over.

The crude product thus obtained was first saturated with chlorine, and then distilled upwards for some hours in a current of dry carbonic acid. On fractionating, the liquid was found to begin to boil at 148°, slowly rising to 154°, between which points the whole of the liquid came over.

A considerable quantity of a solid mass of peachblossom-coloured crystals, consisting of vanadium trichloride, remains behind in the bulb after each distillation. A second preparation of 50 grms. of the pure tetrachloride, gave a constant boiling-point at 152°—154°.

Method 2.—When vanadium oxytrichloride is prepared according to Berzelius's reaction by passing dry chlorine over a mixture of the trioxide and charcoal heated to redness, the distillate possesses a port-wine colour, and it is only by frequent rectifications over sodium that the canary-yellow colour of the pure oxychloride is obtained. This coloration, though ascribed by Schafarik to the presence of traces of vanadic acid, is really due, as I have formerly pointed out, to the presence of a dark-coloured vanadium chloride produced in the reaction, and decomposed on rectification over sodium. This observation, coupled with the fact already made use of to demonstrate the existence of oxygen in the oxytrichloride, viz., that this substance yields up oxygen to red-hot charcoal, points the way to the second method for the preparation of the tetrachloride.

This consists in passing the vapour of the oxytrichloride, together with an excess of dry chlorine, slowly over a long

column of pure sugar-charcoal, heated to dull redness. This operation has to be repeated four or five times before the last traces of oxygen are withdrawn. Even after one distillation the product attains a dark reddish-brown tint, and boils at 152°; but it still contains 1 per cent. of oxygen, and needs three or four very slow repetitions of the process, in order to obtain it perfectly pure. The solid trichloride is always found in the bulb from which the tetrachloride is distilled; but this, if carefully heated, slowly burns away in the excess of chlorine.

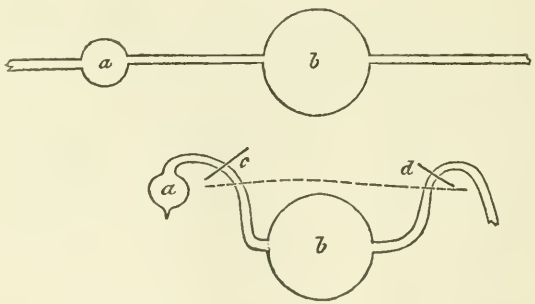
The composition of this chloride is as follows:—

	Calculated.			Mean of Experiments.
V.....	51·3	26·54		26·87
Cl_4	142·0	73·46		73·02
	193·3	100·00		99·89

Vapour-density of Vanadium Tetrachloride.—Owing to the ease with which the tetrachloride decomposes into the trichloride and free chlorine, a solid residue is always left in the bulb when the determination is made by Dumas's method in the ordinary way, and the experimental number is rather too high.

In order to avoid the error arising from the deposition of a solid residue, an arrangement shown in Fig. 1 was used. The tetrachloride was first placed in the small bulb (*a*); the large

Fig. 1.



bulb (*b*) was then submerged, and the oil heated above the boiling-point of the chloride. The chloride was then boiled and the vapour passed through the bulb (*b*), and the tube sealed at *c*. The bulb was then turned round in the oil, so as to bring the point (*c*) below the surface, and the temperature of the bath

allowed to rise above 200° C.; and when the temperature had become constant, the tube was again sealed at *d*.

No. 2.—Weight of bulb and air at 15° C. and under 751 millims..... 19·8945 grms.
Weight of bulb and vapour at 205° and under 758·1 millims..... 20·3015 grms.

Capacity of bulb, 112 cub. centims., residual air, 2 cub. centims. No solid residue was left in the bulb.

Hence the vapour-density is found to be 96·6 (H = 1), or 6·69 (air = 1).

*No.*3.—Another determination made at a higher temperature gave a somewhat lower number, indicating that a portion of the tetrachloride had been decomposed.

Weight of bulb and air 9° C. and under 762 millims..... 24·4722 grms.
Weight of bulb and vapour at 215° C. and under 762 millims. 25·0102 grms.

Capacity of bulb 169·5 cub. centims. No solid residue left in the bulb. Volume of mercury entering the bulb 157 cub. centims.

Hence the vapour-density is found to be 93·3 (H = 1) or 6·48 (air = 1).

Vanadium tetrachloride is a dark brownish-red, thickish liquid, which evolves white fumes when exposed to moist air. Its specific gravity was carefully determined at three temperatures, and found to be:—

at 0° C..... 1·8584
at 8° C.. 1·8363
at 32° C..... 1·8159

It does not solidify at temperatures above − 18° C.; nor does it at this, or any higher temperature, undergo any change of properties on treatment with chlorine. The boiling-point of vanadium tetrachloride is 154° C. (corrected) under a pressure of 760 millims.

Vanadium tetrachloride not only decomposes (as has been stated) on boiling into the trichloride and free chlorine, but the same decomposition takes place slowly at the ordinary temperature of the air. The liquid tetrachloride, sealed up in glass

tubes and exposed to the light, was found on standing for some months to be changed to a dark blackish powder, whilst free chlorine was liberated in such quantity as not only to exhibit its characteristic greenish-yellow colour, but in several cases by its pressure to have burst the tubes. This powder on analysis was found to consist of the trichloride moistened with tetrachloride; on removing this latter liquid in a current of dry carbonic acid at 170°, the pure violet solid trichloride was left behind. Thrown into water the tetrachloride is at once decomposed, yielding a blue solution identical in colour with the liquids obtained by the action of oxalic, sulphurous, or sulphydric acids on vanadic acid in solution, and containing a vanadous salt (derived from the tetroxide, V_2O_4.)

In order to prove that a vanadous salt is formed when the tetrachloride is decomposed by water, the quantity of oxygen which this salt absorbs in conversion into vanadic acid was determined with a standard permanganate solution according to the method described in Part I of these researches (Phil. Trans. 1868, p. 17).

Action of Potassium Permanganate on the Aqueous Solution of Vanadium Tetrachloride.

	(1)	(2)	(3)	(4)
Weight of VCl_4 taken..	0·2375	0·5353	0·4628	0·5687
Cub. centim. of permanganate solution required (1 cub. centim. = 0·00066 grm. oxygen)	15·0	33·2	28·8	35·4
Percentage gain of oxygen found ..	4·17	4·09	4·10	4·09

The calculated percentage gain of oxygen according to the equation

$$2VCl_4 + O + 4H_2O = V_2O_5 + 8HCl \text{ is } 4{\cdot}14.$$

The solution of the tetrachloride in water does not bleach litmus-paper; but if the vapours of the boiling tetrachloride are condensed in water, a liquid is obtained which contains free chlorine, as it bleaches litmus-paper and liberates iodine from potassium iodide. At higher temperatures, as, for instance, when the vapours are led through a red-hot tube, much larger quantities of chlorine are evolved. Vanadium tetrachloride acts violently upon both dry alcohol and ether, giving in the first case a deep green, and in the second a deep red-coloured

liquid. I am at present engaged with the examination of the products of this action.

Action of Bromine on Vanadium Tetrachloride.—Vanadium tetrachloride, heated with excess of bromine in a sealed tube to 180°, yielded a solid mass, which on drying in a stream of carbonic acid at 160°, presented the appearance of the peach-coloured trichloride, and subsequent analysis proved that this body was formed. It is thus seen that, heated in excess of both chlorine and bromine, the tetrachloride splits up into trichloride and free chlorine, so that vanadium does not readily form a pentad compound with the chlorous elements.*

(2.) *Vanadium Trichloride*, $VCl_3 = 157{\cdot}8$.—The trichloride is a solid body, crystallising in splendid peachblossom-coloured shining tables, closely resembling in appearance the crystals of chromium sesquichloride. It is non-volatile when heated in hydrogen, and decomposes when heated in the air, red fumes of oxytrichloride being given off in small quantity, whilst the solid mass glows with absorption of oxygen, forming the pentoxide. Heated in hydrogen it loses, first, one atom of chlorine, forming the dichloride (VCl_2), and afterwards on exposure to a higher temperature, loses the whole of its chlorine, metallic vanadium being left as a grey lustrous powder.

Vanadium trichloride is an extremely hygroscopic substance; it instantly changes colour on exposure to moist air, deliquescing to a dark-brown liquid, which on the addition of a drop of hydrochloric acid becomes green, containing a solution of vanadium trioxide (V_2O_3), or rather of the corresponding hypovanadic salts.

The trichloride is obtained (1) by the slow decomposition of the tetrachloride at the ordinary atmospheric temperatures, (2) by the decomposition of the tetrachloride at its boiling-point, (3) together with dichloride, when the vapour of the tetrachloride is passed mixed with hydrogen through a red-hot tube. Method No. 2 is that which yields the trichloride in largest quantity and in the purest state, large quantities of the peach-coloured crystals remaining behind in the bulb-retort; and these only require heating in a current of carbon dioxide at 160° in order to yield the pure trichloride.

* The only other case of an element of a decidedly triad character yielding compounds of a tetrad nature, appears to be the nitrosyl-dichloride, $NO\,Cl_2$, of Gay-Lussac, and the corresponding bromine compound, $NO\,Br_2$, discovered by Landolt.

Its composition is as follows :—

	Calculated.		Mean of Experiments.
V	51·3	32·5	 32·57
Cl_3	106·5	67·5	 67·42
	157·8	100·0	 99·99

When the trichloride is thrown into water it does not at once dissolve, the peachblossom-coloured crystals floating in the liquid; these, however, gradually dissolve, forming a brown-coloured solution, which on addition of a drop of acid turns to a bright green colour, identical in tint with the liquid obtained by reducing vanadic acid in solution with nascent hydrogen evolved by magnesium, and containing a hypovanadic salt. Like the solution obtained by reduction, the green-coloured solution of the trichloride absorbs oxygen on standing, passing into the blue solution of the vanadous salts. A solution of hypovanadic salt obtained by dissolving 0·293 grm. of trichloride in water required 45 cub. centims. of permanganate solution in order to oxidize it completely (1 cub. centim. permanganate = 0·00066 grm. oxygen). Hence the quantity of oxygen needed to oxidize the solution was 10·10 per cent. (on the trichloride), whilst that required by the formula $2VCl_3 + O_2 + 3H_2O = V_2O_5 + 6HCl$ is 10·14 per cent.

The specific gravity of vanadium trichloride at 18° is 3·00. Vanadium trichloride dissolves readily in absolute alcohol, forming a greenish-blue solution; in ether it also dissolves, giving a green-coloured solution.

(3.) *Vanadium Dichloride*, $VCl_2 = 122·3$.—Vanadium dichloride is a solid body crystallising in fine bright apple-green plates, having a micaceous lustre and an hexagonal form. It is prepared by passing the vapour of vanadium tetrachloride mixed with dry and pure hydrogen through a glass tube heated to dull redness. If the distillation of the tetrachloride be conducted slowly, and the mixture of vapour and hydrogen brought at once into the heated portion of the tube, the pure dichloride is deposited in light pearly scales, which can easily be shaken out of the tube. If the operation be conducted too quickly, or if the hydrogen be not present in large excess, a considerable quantity of the peach-coloured trichloride is formed in the anterior portion of the tube, and the green crystals of dichloride collect in one spot and are fixed firmly to

the glass. If the temperature be raised to a bright red heat during the preparation, the dichloride is further reduced, a black crystalline powder containing a mixture of lower chlorides and metal being produced, whilst the glass tube becomes opaque, with formation of the silicon-vanadium compound. When heated for a long time in a platinum-boat in a current of pure and dry hydrogen, the dichloride loses all its chlorine, metallic vanadium being left in the form of bright greyish-white lustrous metallic grains.

The composition of the dichloride is as follows:—

	Calculated.		Mean of Experiments.
V	51·3	41·95	 42·16
Cl_2	71·0	58·05	 57·88
	122·3	100·00	 100·04

Vanadium dichloride, when heated in hydrogen or in carbon dioxide, does not volatilize without decomposition. It is extremely hygroscopic, instantly absorbing moisture from the air, deliquescing to a brown liquid; a portion of this chloride exposed to the air for five minutes gained 4 per cent. in weight, and in standing for sixteen hours the increase amounted to 50 per cent. When thrown into water the dichloride does not at once dissolve, the scales floating on the water without becoming wet; soon, however, they dissolve, forming a violet-coloured liquid, identical in tint with the solution of hypovanadous sulphate obtained by reducing a solution of vanadic acid in sulphuric acid by hydrogen evolved from zinc or sodium. Like this latter liquid, the solution of the dichloride in water acts as a very powerful reducing agent, bleaching litmus and indigo solutions.

A solution of hypovanadous salt obtained by dissolving 0·2875 grm. of vanadium dichloride in water required 81·8 cub. centims. of permanganate solution completely to oxidize it (1 cub. centim. = 0·00066 grm. oxygen). Hence the percentage (on the dichloride) of oxygen needed to oxidize the solution was 18·78, whereas the formula $2VCl_2 + O_3 + 2H_2O = V_2O_5 + 4HCl$ requires 19·6 per cent.; the difference between the found and calculated numbers is due to the great difficulty of preventing the solution absorbing some little oxygen during the analysis, which must of course be conducted in an atmosphere of carbon dioxide. When the dichloride placed in a platinum

boat is heated to whiteness in a current of dry ammonia, dense fumes of ammonium chloride are given off, and on cooling after an hour's heating, the boat contains vanadium mononitride in bronze-coloured pseudomorph crystals, which exhibit by reflected light a bright metallic lustre.

The specific gravity of vanadium dichloride at 18° C., is 3·23, as a mean of two well-agreeing determinations. Vanadium dichloride dissolves slowly in alcohol and in ether, giving in the one case a blue and in the other a greenish-yellow solution.

Metallic Vanadium, V = 51·3.—From what we now know of the character of vanadium, we learn without surprise that the metal cannot be prepared in the free state by any of the methods given in the books.

Berzelius (Pogg. Ann. vol. xx, p. 1) obtained a brilliant metallic scale by heating the oxytrichlorides, placed in a bulb-tube, in an atmosphere of ammonia; but this substance, as Schafarik observes, is mononitride, and not metal. The great Swedish chemist also states that the metal can be prepared in a pulverulent form by exploding fused vanadic acid with potassium. The black powder which is obtained by lixiviating the fused mass is, however, not metal but an indefinite mixture of oxides. Schafarik (Ann. der Ch. und Pharm. vol. cix, p. 97) describes as metal the brownish-yellow lustrous crystals obtained by passing the vapour of the oxytrichloride mixed with hydrogen through a red-hot tube. The body thus prepared, as I have already shown, is not the metal, but a mixture of the lower oxychlorides of vanadium.

Johnston (N. Edin. Journ. of Sc., vol. v, pp. 166, 318) obtained a hard brittle metallic globule by reducing vanadic acid with carbon at a white heat; this was certainly not metallic vanadium, probably the alloy with silicon.

Although it appeared unlikely that any compound of vanadium containing oxygen would yield the metal by direct reduction, I have nevertheless repeated the above experiments, but without success. In order to test the second method proposed by Berzelius, the fused pentoxide was mixed with excess of sodium, and the mixture heated in a closed wrought-iron crucible; after the explosion the black mass was washed until free from alkali. A black powder is thus obtained which glitters when suspended in water, and this powder on oxidation

only gained 16 per cent., showing that it contained even more oxygen than the trioxide.

Johnston's experiment was also repeated by exposing a mixture of trioxide, charcoal, and oil contained in a graphite crucible for several hours to the heat of a wind-furnace in which manganese can be fused. Not a trace of either a bead or metallic powder was obtained, and the black powder gained on oxidation only 16 per cent.

In order to ascertain whether under other circumstances the trioxide can be reduced, a portion of this oxide was heated to whiteness in a current of hydrogen, both when alone and mixed with excess of sodium; in neither case was the metal formed, a black residue of oxide remaining behind in the boats. The trioxide heated in a graphite crucible to bright redness with magnesium also yielded a black powder consisting of mixed oxides.

Another reaction consisted in passing the vapour of oxytrichloride mixed with hydrogen over metallic sodium heated in a porcelain boat; a black shining powder was thus obtained, which after lixiviation and drying was burnt to vanadium pentoxide, and gained only 11 per cent. in weight.

The only methods which promised possible results were:—

1. The reduction of vanadium chloride (free from oxygen) in hydrogen gas.

2. The reduction of the mononitride in a current of hydrogen.

The first of these methods has been found to be successful, the second does not appear to yield the metal; for in two experiments in which the mononitride was ignited in a platinum-tube to whiteness in a current of hydrogen, in one case for $3\frac{1}{2}$, and in another for 2 hours, the loss of weight was only 8·8 and 8·4 per cent. respectively, whereas the nitride must lose 21·4 per cent. when converted into the metal.

Reduction of the Metal from Vanadium Dichloride in Hydrogen.—The only method by which it has been found possible to obtain metallic vanadium is by the reduction of a chloride free from oxygen, in an atmosphere of perfectly pure hydrogen. Although this process appears simple enough, yet there is, I believe, no metal more difficult to obtain than vanadium.

This arises from the circumstance that while vanadium appears to be stable at ordinary atmospheric temperatures, it

absorbs oxygen at a red heat with the greatest avidity, and that therefore every trace of air or of moisture must be excluded. Another difficulty consists in the preparation of sufficiently large quantities of the solid chlorides free from oxygen or moisture, as also in the length of time necessary in order to reduce these chlorides in hydrogen at a red heat, during which time diffusion (which can never be wholly prevented) brings traces of oxygen in contact with the heated metal. Then, again, the destructive action of the metal on glass and porcelain prevents these substances being used to contain the metal, whilst tubes of platinum and wrought iron become so porous at a red heat as to admit sufficient oxygen to convert the whole vanadium into trioxide. The only means which can be adopted is to heat the chloride in a platinum boat placed in a porcelain tube.

A laborious series of preliminary experiments on the reduction of the metal in this way proved that, in order to obtain a substance even approaching to the metal, many precautions must be taken; whilst they showed that, in spite of every care, it is extremely difficult to obtain the metal itself. Thus no fewer than ten experiments made by different modifications of this method yielded mixtures of metal with more or less oxide, of which the analyses showed an increase on complete oxidation varying from 60 to 67 per cent., that for pure metal being 78, whilst in every case in which the pure metal was prepared, a considerable quantity of black sesquioxide was formed at the end of the boat nearest the inflow of hydrogen, showing that the source of error lay in the presence of diffused oxygen.

The apparatus which, after many alterations, was found best adapted for the preparation of the metal is represented on Fig. 2 (p. 356).

It consists of a hydrogen generator (A) yielding a stream of hydrogen, which can be kept constantly passing through the wash-bottles day and night for a week at a time, by occasionally adding fresh acid to the upper bottle and drawing off the zinc-sulphate solution from the lower bottle by the catouchouc tube. The first wash-bottle contains a solution of lead acetate, the second silver nitrate, and the other three boiled sulphuric acid. In order to remove any trace of oxygen which may have accompanied the hydrogen arising either from diffusion or from air absorbed in the dilute acid used, a tube (C D) is attached to the

end of the last washing bottle; the first portion of this tube contains a quantity of platinum sponge (C), which is heated to redness during the whole time the hydrogen is passing through the apparatus, whilst the further portion of the tube D is filled with phosphorus pentoxide and plugs of cotton-wool. The greatest care was taken to have all caoutchouc stoppers and joints made as tight as possible with copper wire and paraffin. At right angles to the drying tube (C D) is placed the reducing arrangement shown in the lowest part of the drawing. This consists of a porcelain tube (E E′) placed in a Hofmann's furnace, and protected in the central portions, where it is heated by an outer casing of sheet iron. The porcelain tube is connected with the hydrogen apparatus by means of the wide glass tube (F F′) provided with the tubulus (G), and narrowed down to join the drying-tube at F′. The joint between the porcelain and glass tubes is made of seamless caoutchouc well wired, and covered by an outer short glass cylinder, the space between the tubes and the cylinder being filled either with mercury or fused paraffin, and a similar joint is placed at the further end of the porcelain tube.

The introduction of the anhydrous dichloride without exposure to the air is effected by means of the tubulus (G), the dichloride being contained in the bent tube (H) in which it was prepared and sealed up in hydrogen. After the whole arrangement has been set up, the platinum boat being in position as shown in the figure, hydrogen is allowed to pass through the apparatus for twelve hours, to dry it completely and clear out the air; the caoutchouc stopper of the tubulus is then withdrawn, and the end of the tube containing the dichloride cut off, and the tube and stopper quickly replaced, so that the crystals lie in the horizontal portions of the tube. The bent tube is next so turned in the stopper that the crystals of dichloride fall out and are collected in the platinum boat placed below. This boat, charged with dichloride, is then withdrawn into the centre of the porcelain tube by means of the platinum wire, the end of which (W) passes through a small hole in the caoutchouc tube at the end of the apparatus. As soon as the boat is in position, the wire is cut off short at the end of the glass tube, a proper joint made, and an exit-tube attached, dipping under sulphuric acid.

Before the porcelain tube is heated, the caoutchouc stopper of

the tubulus is surrounded by a bath of paraffin, and the hydrogen is allowed to bubble through for six hours. The tempera-

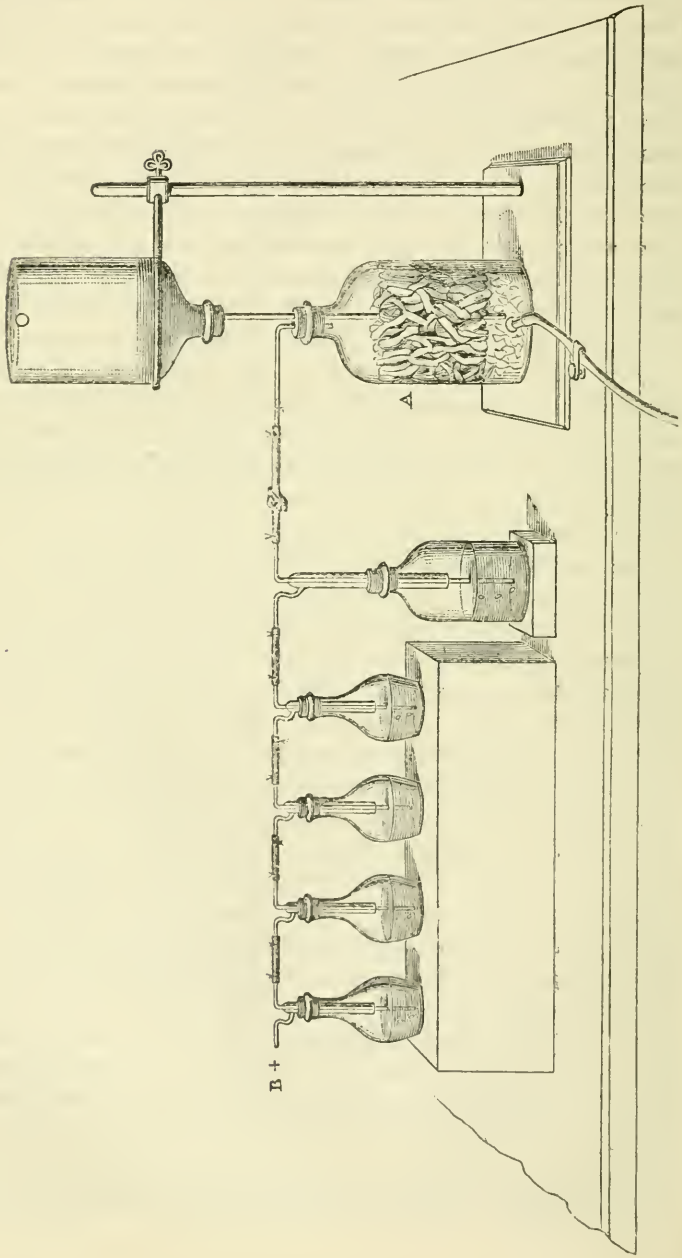


Fig. 2.

ture of the porcelain tube is then gradually raised to the highest point (a bright red heat) which the Hofmann's furnace will yield, and kept constant until the reduction is complete. Torrents of hydrochloric acid gas at once come off, and the process must be continued for some hours after the last trace of acid can be detected in the hydrogen. The process lasts from forty to eighty hours, according as the quantity of dichloride employed varies from 1 to 3 or 4 grms.

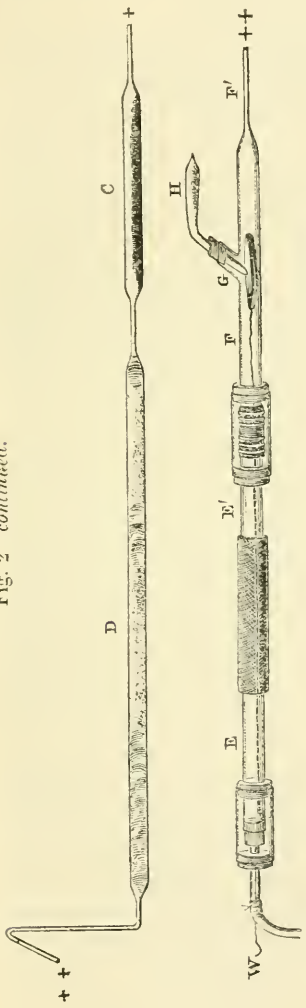


Fig. 2 *continued.*

Metallic vanadium prepared by reduction from the dichloride in hydrogen is a light whitish grey-coloured powder, which under the microscope reflects light most powerfully, and appears as a brilliant crystalline metallic mass, possessing a silver-white lustre. It is remarkable that vanadium thus prepared does not oxidize or even tarnish in the air at the ordinary atmospheric temperature, nor does it decompose water at the ordinary temperature, and it may be moistened and dried *in vacuo* frequently without gaining in weight. Vanadium is neither volatile nor fusible when heated to redness in hydrogen. When the powdered metal is thrown into a flame, or rapidly heated in an excess of oxygen, it burns with the most brilliant scintillations, and when slowly heated in a current of air, it glows brightly with absorption of oxygen, forming in the first place a brown oxide (V_2O or V_2O_2); and on further heating, this oxide again glows, and passes through the black trioxide and blue tetroxide to pentoxide. The metal-powder is not magnetic, and it could not be pressed into a coherent form. Its specific gravity at 15° was found to be 5·5 as a mean of three determinations. The

metal is not attacked by hydrochloric acid,* either when hot or cold; neither strong nor dilute sulphuric acid acts on the metal in the cold, but when heated with the strong acid the metal slowly dissolves, giving a greenish-yellow solution. Hydrofluoric acid dissolves the metal slowly with evolution of hydrogen, and formation of a green solution, whilst nitric acid of all strengths oxidizes it with violence, evolving nitrous fumes, and forming a blue liquid. Both hot and cold solutions of caustic soda are without action on the metal, but when it is fused with the hydroxide, hydrogen is evolved and a vanadate formed.

The metallic powder obtained by reduction contains a quantity of combined or absorbed hydrogen, the amount of which frequently rose up to 1·3 per cent. The weight of this hydrogen must be determined by burning the metal placed in a platinum boat in a glass tube, through which first a stream of dry air, and afterwards of pure oxygen is passed. A drying-tube placed in front of the combustion-tube, gives the weight of water formed.

Metallic vanadium burns in excess of dry chlorine, forming the tetrachloride.

Heated in an atmosphere of pure nitrogen, metallic vanadium at once absorbs this gas, and is converted into mononitride.

Vanadium attacks all glass or porcelain in which it is heated, a compound of silicon and the metal being formed. This compound coats all tubes of glass or porcelain in which the chlorides have been heated and reduced, as a grey lustrous metallic mirror, the formation of which renders the tubes very brittle and liable to crack. The silicon compound is not attacked by hydrochloric, and only slightly by nitric acid, but it tarnishes after a time on exposure. The metal also forms an alloy with platinum. All the platinum boats and tubes in which the reduction has been made are found after the operation to be completely saturated with vanadium, and require to be frequently ignited in the air, and as often boiled out with a solvent for vanadic acid, before they can be freed from the absorbed metal. If the platinum be frequently used for the reduction without this purification, it becomes brittle and dark-coloured from absorption of metal in quantity.

* Hydrochloric acid readily dissolves the trioxide.

XXVII.—*On the Precipitation of Solutions of Ammonium Carbonate, Sodium Carbonate, and Ammonium Carbamate by Calcium Chloride.*

By Edward Divers, M.D.

I have made some experiments on the behaviour of ammonium carbonate with calcium chloride as compared with that of sodium carbonate and of ammonium carbamate with the same substance.

The results of these experiments are principally of interest as supplying a characteristic reaction for the carbamate, and from the evidence they afford of the insufficiency of the commonly received explanation suggested by Kolbe* of the fact first pointed out by Vogel,† that solutions of carbonic anhydride are only imperfectly, or not at all, precipitated in the cold by a mixture of calcium chloride and ammonia. This fact Kolbe considers to be due to the production of some calcium carbamate which remains in solution.

That carbamate is first formed when carbonic anhydride meets ammonia in solution is indeed certain, since as I have recently pointed out, crystallised ammonium carbamate can be readily obtained by acting on ammonia in aqueous solution by carbonic anhydride. But then the behaviour of ammonium carbonate, or even, to a limited extent, of sodium carbonate with the mixed ammonia and calcium chloride I find to be precisely that which in the case of carbonic anhydride is attributed to ammonium carbamate.

If to a mixture of ammonia-water and solution of calcium chloride a very little dilute solution of ammonium carbonate is added with agitation, a gelatinous precipitate forms, and immediately after re-dissolves. On standing, a precipitate more or less gelatinous again forms, but only very gradually, which slowly assumes the chalky condition, particularly if the solution be freely diluted with water. If the calcium chloride and ammonia

* Handwörterbuch der Chemie, vol. i, suppl., p. 157.

† Recherches Analytiques sur le Corail Rouge, Annales de Chimie, vol. lxxxix, p. 113 (1819); Ueber eine unsichere Methode das Verhältniss des Kohlensäure Gases bei Analysen zu bestimmen, Schweigger's Journal für Chemie und Physik, vol. xxxiii, p. 204 (1821).

are added to a larger proportion of ammonium carbonate, but still in marked excess, some of the gelatinous precipitate first formed is permanent, but more precipitate is gradually deposited. It is, with either mixture, days before precipitation is so far complete that the supernatant fluid no longer gives a precipitate on being heated.

The addition of the mixed ammonia and calcium chloride solutions to a very little exceedingly dilute solution of sodium carbonate, throws down a gelatinous precipitate, which redissolves nearly or entirely, and forms a solution which only after some time deposits a chalky precipitate. Added, still in considerable excess, to a larger proportion than in the last case of very dilute solution of sodium carbonate, the mixed reagent causes a permanent, at first gelatinous, afterwards chalky, precipitate, but even in three hours the clear supernatant fluid sometimes yields a good precipitate when heated.

So that the action of sodium carbonate is the same in kind as that of ammonium carbonate and differs only in degree; while the behaviour of the latter salt with the excess of calcium chloride and ammonia is sensibly and practically identical with that of a solution of carbonic anhydride with the same reagents.

As regards the precipitation effected by heat in the mixture of excess of calcium chloride and ammonia with ammonium carbonate, this is only slowly produced if the mixture is strong in ammonia and calcium chloride.

If in the previous experiments the calcium chloride is used unmixed with caustic ammonia, the carbonates of ammonium and of sodium show at first each the same behaviour as before; but even with the ammonium salt the second precipitation of chalky carbonate is now not long in setting in, and after the supernatant fluid has stood about two hours, it fails to give a precipitate when heated, while with the sodium salt the reprecipitation of calcium carbonate takes place almost immediately, and the supernatant solution fails in a very short time to yield a precipitate on boiling.

It therefore appears that caustic ammonia in the presence of excess of calcium chloride very considerably retards the precipitation of calcium carbonate.

Fragments of a cake of ammonium carbamate, obtained by distillation, and almost pure, except superficially, were washed with a little water to remove the outer portions, and dissolved

in cold water so as to form a dilute solution. Some of this solution treated without delay with excess of calcium chloride, gave a slight precipitate at once. In two hours the supernatant fluid gave a very slight precipitate on being heated, but in four hours ceased to give any at all. A solution of ammonium carbonate of about the same strength would have given very much more precipitate at first, and the supernatant fluid would have failed to give when heated any precipitate in two hours or less. Ammonium or calcium carbamate, therefore, very soon passes into the state of carbonate in the presence of calcium chloride when caustic ammonia is absent. The presence of ammonia in addition materially impedes this change. Thus, when the above experiment with the carbamate was repeated with the modification of adding caustic ammonia, no precipitate appeared for hours, and in eight hours only a very slight one, while a day afterwards the clear supernatant fluid gave when heated a very copious precipitate. Other and decisive evidence that ammonia retards the conversion of ammonium carbamate into carbonate, has been given in my paper on the combinations of carbonic anhydride with ammonia and water: further evidence will also be given presently.

When, therefore, a solution of carbonic anhydride is treated with excess of calcium chloride and ammonia, it first forms carbamate which slowly passes into carbonate; but its imperfect precipitation as carbonate is essentially due to the fact that the excess of calcium chloride and ammonia greatly retards the complete precipitation of calcium carbonate in the cold.*

When ammonium or sodium carbonate is added in excess to calcium chloride, the action of ammonia is very different. A moderately strong solution of ammonium carbonate mixed with a very little dilute solution of calcium chloride gives, in the absence of ammonia, a gelatinous precipitate redissolving on agitation, as Storer has particularly pointed out.† This solution, according to my experiments, soon deposits the calcium

* According to Storer (First Outlines of a Dictionary of Chemical Solubilities, 1864, p. 110), carbonic anhydride produces no precipitate with the mixed solution of calcium chloride and ammonia, *even when the mixture is boiled,* in presence of excess of ammonium chloride. This statement I have not been able to confirm. Carbonic anhydride solution, mixed with ammonia and ammonium chloride, gives at once a well-marked precipitate when heated with calcium chloride, whether this has been added in excess, or in quantity insufficient to precipitate it all.

† Op. cit., p. 110.

carbonate in the chalky state, and in less than an hour the filtered solution gives no precipitate when boiled. In the presence of caustic ammonia it becomes almost impossible to add the smallest quantity of calcium chloride without causing an immediate gelatinous precipitate, permanent on agitation, and the mother-liquor soon fails to give a further precipitate on boiling. So that in the presence of ammonium carbonate, ammonia determines the precipitation of calcium carbonate instead of impeding it, as it does in the presence of calcium chloride. The greater insolubility of calcium carbonate in solution of ammonium chloride or nitrate in the presence of ammonium carbonate and ammonia has been pointed out by Fresenius,* and also its much greater insolubility in ammonia-water than in pure water.† His experiments, however, refer to the crystalline precipitated calcium carbonate: the above experiment shows the great insolubility, in the presence of ammonium carbonate and ammonia, of calcium carbonate in its gelatinous and, under other circumstances, much more soluble condition. It is to be plainly inferred from the statements in some of the best works on qualitative analysis that, in the precipitation of calcium salts by ammonium carbonate, ammonia is added merely to ensure the absence of any acid carbonate; but it is evident that the presence of free ammonia is necessary to render the precipitation instant and complete.‡

The reactions of sodium carbonate used in excess, both in the presence and absence of ammonia, are quite similar to those obtained with ammonium carbonate.§

Ammonium carbamate solution when treated with less than its equivalent of calcium chloride, very soon yields a precipitate, and in about two hours the filtered solution gives no further precipitate on being heated. The reaction is therefore the same as when the calcium chloride is added in excess. When ammonia is added, the calcium chloride gives an instantaneous, but slight, precipitate with excess of the solution of the carbamate. The precipitate increases very slowly on standing, and the supernatant solution a day after gives a further copious

* Quantitative Analysis, fourth English edition, p. 107. † Op. cit., p. 164.

‡ Ammonia quickens the precipitation of ammonio-magnesian carbonate.

§ The sodium carbonate used to determine this fact was pure, and was dissolved in cooled, freshly-boiled water, so as to ensure the absence of any acid carbonate, by neutralizing which, it might otherwise be said, the ammonia produced its effect.

precipitate on boiling. The immediate precipitation is undoubtedly due to the presence of ammonium carbonate; and the very slow further precipitation of the solution affords another proof how slowly the carbamate changes into carbonate, in presence of free ammonia.

The distinguishing reaction, therefore, between ammonium carbamate and ammonium carbonate is that, added *in excess* to ammonia and calcium chloride, the carbamate precipitates the calcium very slowly, while the carbonate precipitates it immediately.

The fact that the carbamate gives a more soluble calcium salt than the carbonate does, is of itself hardly of any use as a test, because, firstly, the apparent solubility depends so much on the strength of the solution; and secondly, except in the presence of ammonia, the carbamate so rapidly passes into carbonate.

The gelatinous precipitate (calcium carbamate?) produced in solution of ammonium carbamate by excess of calcium chloride, can be dissolved by sufficient water added immediately. Water also sensibly dissolves a precipitate of gelatinous calcium carbonate, but not at all to the extent that it does the former precipitate. The carbamate precipitate has appeared to me to be less soluble in calcium chloride solution than in pure water, but I cannot speak with much certainty on this point.

Concentrated solutions of ammonium carbonate and sodium carbonate act in a special way with very concentrated solution of calcium chloride. When a concentrated solution of the ammonium salt is treated with a very little saturated solution of calcium chloride and agitated, a precipitate is produced, almost invisible at first, which rapidly subsides in gelatinous flocks; further addition of calcium chloride fills the liquid with the precipitate, but still not so as to gelatinize and solidify the liquid, as it would do were the solutions much less concentrated; when the calcium chloride is added to large excess, the precipitate already formed changes its appearance, becoming white and opaque, and not unlike silver chloride. When to a saturated solution of calcium chloride a drop of saturated, or very concentrated solution of ammonium carbonate is added with agitation, the precipitation is also immediate and scanty, and the precipitate sinks rapidly, but it is in curdy, or rather thready, slightly translucent particles. The form of the precipitate is

probably to be accounted for by the fact that the solutions mix with difficulty. The supernatant fluid, containing the excess of calcium chloride, can easily be decanted from the precipitate, and this can be washed by decantation; by such treatment it undergoes little change in appearance, beyond getting more opaque, and seems to be nothing but calcium carbonate. If the carbonate be added in larger quantity to the calcium solution, a good deal of gelatinous precipitate forms, but not to anything like the extent it would do with more dilute solutions; in fact, by adding water in moderate quantity to the mixture, the whole quickly becomes solid. If the calcium chloride used in the above experiments be first charged with ammonia, the results appear to be the same. A concentrated solution of sodium carbonate substituted for that of ammonium carbonate, gives quite similar results.

The fact that a very concentrated ammoniacal solution of ammonium carbamate gives with a saturated solution of calcium chloride a precipitate which is soluble in water, and which has a composition indicating that it is either calcium carbamate or ammonio-calcium carbonate, has been noticed in my paper on the combinations of carbonic anhydride with ammonia and water.

Addenda et Corrigenda.

[*On the Combinations of Carbonic Anhydride with Ammonia and Water.*]

Page 187. Precipitation of ammonium carbonate by ammonia. Sodium carbonate is also precipitated by ammonia, according to Margueritte, who patented the precipitation in 1855.

„ 199. Formation of acid ammonium carbonate by the union of carbonic anhydride, ammonia, and water. Gossage patented in 1854 the production of the acid carbonate by passing ammonia and carbonic anhydride into water as a means of utilizing bye-products in the manufacture of sodium carbonate from common salt by acid ammonium carbonate. Laming has patented the formation of carbonate of ammonia in the same way.

„ 212, line 18 from bottom; for "+" read "and."

„ 236, line 5 from top; after "grm." insert "of (*b*)."

„ „ 7 „ "grms." „ „

„ 249. Behaviour of the commercial carbonate with potassium carbonate. Schorz, following Schöffer, prepares the acid sodium carbonate and

caustic ammonia by distilling together 50 parts of dry sodium carbonate, 15 parts of crystalline sodium carbonate, and 41 of commercial carbonate of ammonia. Richardson and Watts' "Chem. Techn.," 2nd edition, vol. I, part iii, p. 316.

Page 251. Behaviour of the commercial carbonate with common salt. The production of acid sodium carbonate and sal-ammoniac, by adding either the acid ammonium carbonate, or the commercial carbonate, or carbonic anhydride and ammonia to a solution of common salt, has in one form or another been the subject of patents granted to Dyar and Hemming in 1838, to Waterton in 1840, to Schlösing in 1854, to J. H. Johnson in the same year, to Gossage in 1855, to Bellford in the same year, and to Schlösing and Rolland in 1858.

„ 256, line 11 from bottom, for "carbonate" read "carbamate."

„ 264 „ 20 „ top „ "10" read "8·5."

„ 265 „ 22 „ „ „ „

„ „ Formation of the commercial carbonate from the acid carbonate by distillation. This process was patented in 1846 by F. Clarke Hills.

„ 267. Composition of the most remote product of the distillation of the commercial carbonate. This is almost exactly that of a mixture of one part of the commercial carbonate with three parts of the half-acid carbonate, the calculated numbers for which are—carbonic anhydride, 50·41; ammonia, 26·87; and water, 22·72. Composition of the product next to the most remote. This is almost exactly that of a mixture of three parts half-acid carbonate with four parts of commercial carbonate, the numbers for which are—carbonic anhydride, 52·83; ammonia, 29·27; and water, 17·90. It is more than probable that the half-acid carbonate in these mixtures was, when first formed the normal carbonate, in accordance with the statement of Dalton. The correction at page 181, line 18 from bottom, made in the previous list of *corrigenda*, is therefore not required.

„ 268. Composition of the product described at the bottom of the page. This is most satisfactorily interpreted as that of a mixture of four parts commercial carbonate, one part carbamate, and 2½ per cent. water, the calculated numbers being—carbonic anhydride, 54·72; ammonia, 33·83; and water, 11·45.

„ 270. Composition of the warty inner surface. This is better represented as that of a mixture of two parts commercial carbonate with three parts half-acid carbonate, the numbers being—carbonic anhydride, 51·54; ammonia, 27·99; and water, 20·41. Composition of the product deposited next the heat, probably somewhat altered. This corresponds to that of a mixture of four parts commercial carbonate, seven parts half-acid carbonate, and two parts acid carbonate, the numbers being—carbonic anhydride, 51·94; ammonia, 26·77; and water, 21·29. The formula $(CO_2)_3(OH_2)_3(NH_3)_4$ is equal to $\frac{1}{2}$ $[(CO_2)_2OH_2(NH_3)_3 + (CO_2)_3(OH_2)_4(NH_3)_4 + CO_2OH_2NH_3]$. The preceding modifications in the representation of the composition of the products obtained by distilling the commercial carbonate will probably serve to justify more clearly the deductions drawn from the analyses.

„ 271 line 9 from top, for "acid carbonate," read "half-acid and acid carbonates."

„ „ Distillation of the commercial carbonate with water. Gossage patented

in 1855 the production of the acid carbonate and a residual solution of the normal carbonate by distilling an aqueous solution of the commercial carbonate.

Page 273. The single substances produced by condensing mixtures of carbonic anhydride, ammonia and water. Among these ought probably be placed the half-acid carbonate.

„ 274. line 16 from bottom, for "of equal volumes of water-vapour and ammonia," read "of water-vapour and ammonia in atomic proportions."

XXVIII.—*On the Manipulation of Assays of Gold and Silver Bullion.*

By Charles Tookey, Assayer in the Japanese Imperial Mint, formerly in the Royal Mint, Hong Kong.

In the year 1854, in conjunction with the late Mr. T. H. Henry, I began to work out an investigation relative to certain methods by which ordinary assays of gold bullion might be made with greater rapidity than was then practicable.

The number of separate processes, from the first weighing in of a piece of gold bullion to the second weighing out before its value can be ascertained, are well known to all assayers. The object which we had in view was to treat a batch of assays simultaneously, instead of handling them in rotation and individually, as by the ordinary method.

The first step was to substitute a perforated tube holding the assay for the parting flask, which should allow of free access of the nitric acid used for separating the gold and silver. The original tube was made by inserting a circular piece of perforated platinum foil near one end of the neck of a pear-shaped parting flask.

By providing these tubes with a shoulder near the upper end, they could be easily supported by a porcelain tile having circular holes, the tubes and holes being numbered, so that each assay occupied the same relative position throughout the operations; the whole arrangement could then be lowered, till the assays were sufficiently immersed, into one vessel of nitric acid of proper strength, boiled for the requisite time, taken out, boiled a second time in stronger acid, washed, dried, and annealed, thus managing the whole as one assay, and thereby saving a considerable amount of time.

I need not enter here into the various points for consideration in the application of this system; I have simply wished to show how it originated, and to mention that the apparatus is now made wholly of platinum.

One of the operations in the assay of silver bullion by the "dry method" consists in carefully hammering the buttons after they have been detached from the cupels, and then brushing them, in order to remove adhering portions of bone-ash, which has been saturated with oxide of lead during the process of cupellation.

This operation, like the individual system in gold assaying, occupies much time, and is certainly open to objection, especially when the bullion is not of high standard, because the hammering squeezes up the porous under-surface of the buttons, and causes them to retain mechanically portions of bone-ash, which no amount of brushing will wholly remove.

It may be admitted here that as all the assay buttons, including the "checks" which are used to control the results, are treated in a similar manner, the amount of error is reduced to a minimum. At the same time a mechanical operation, which can seldom be exactly the same in any two cases, must yield to a more certain process, which in its action is uniform throughout.

In the Royal Mint at Hong Kong, I substituted another method for cleansing the assay buttons; when systematised it occupies much less time, and is more satisfactory and certain in its action than the old process.

The silver buttons, after being detached from the cupels by means of forceps, are transferred to a platinum plate, having depressed perforated cavities arranged and numbered to correspond with the cupels in the muffle. The buttons are placed in their respective places with the underside uppermost, and by means of a handle of platinum wire attached to the plate, the whole is immersed in pure hydrochloric acid (in the proportion of one part of strong acid to two of water), the acid is heated sufficiently (not boiled), and when all the bone-ash, &c., has been dissolved, the plate is lifted out by its handle, washed first in hot water acidulated with hydrochloric acid, and, lastly, in pure water; the plate is then drained by being placed upon porous paper, and dried perfectly over a gas or

spirit lamp. Two assay buttons, one of which has been subjected to the ordinary treatment by the hammer and brush, and the other to the process which I have described, will have distinct appearances under a magnifying glass, and from the former, phosphate of lime may, in most cases, be separated and identified.

XXIX.—*On some new Bromine Derivatives of Coumarin.*

By W. H. Perkin, F.R.S.

In my endeavours to get a clearer insight into the constitution of coumarin, I have lately been studying the action of bromine upon it, and although my results do not at present throw much fresh light upon the subject, still I have thought it as well to bring a short account of my experiments before the Society.

Bromine combines readily with coumarin, without evolution of hydrobromic acid in appreciable quantities; the product, however, varies according to the manner in which the experiment is performed. I have not as yet investigated all the products of this reaction, but have obtained the following results.

On adding about fourteen parts of powdered coumarin to sixteen parts of bromine, disulphide of carbon being previously added to both bodies, the resulting solution when allowed to evaporate spontaneously leaves a crystalline residue.

This can be freed from secondary products, first, by washing with a little cold alcohol, and then crystallising from the same solvent. This latter operation should be conducted as quickly as possible, and with the use of but little heat.

The analysis of specimens of the product dried in vacuo gave the following numbers:—

I.	·7873	grm.	of substance gave
	·9685	,,	AgBr.
II.	·3910	,,	substance gave
	·5051	,,	CO_2, and
	·0759	,,	H_2O.
III.	·3645	,,	substance gave
	·4784	,,	CO_2, and
	·0701	,,	H_2O.

These numbers give percentages agreeing with the formula—

$$C_9H_6O_2Br_2,$$

as the following comparisons will show—

	Theory.		Experiment.		
			I.	II.	III.
C_9	108	35·29	—	35·23	35·79
H_6	6	1·96	—	2·16	2·14
O_2	32	10·46	—	—	—
Br_2....	160	52·29	52·35	—	—
	306	100·00			

This body is, therefore, formed by the direct union of bromine and coumarin. I propose to call it *dibromide of coumarin.*

Dibromide of coumarin fuses at about 100° C., with partial decomposition, and when further heated gives off bromine vapour. It is easily soluble in alcohol, and crystallises from it in transparent oblique prisms. When boiled with alcohol it quickly decomposes; the same thing takes place when its alcoholic solution is exposed to light, the bromine apparently acting upon the solvent, leaving coumarin in solution. It is also soluble in ether and disulphide of carbon.

When a mixture of bromine and coumarin, in the proportion of two parts of the former to one of the latter, both being previously mixed with disulphide of carbon, is heated in a sealed tube to about 140° C. for a few hours, most of the bromine disappears, but not all, the liquid being still of an orange-red colour. On cooling, the resulting product crystallises, generally showing two kinds of crystals, and on opening the tube large quantities of hydrobromic acid are given off.

The contents of the tube, after the disulphide of carbon has been allowed to evaporate, dissolve in boiling alcohol, and the solution on cooling deposits a quantity of crystals. These, when purified by three or four recrystallisations from alcohol, gave the following numbers on analysis. The substance was dried at 100° C.—

I. ·3356 grm. of substance gave
·4178 „ AgBr.
II. ·2855 „ substance gave
·3751 „ CO_2, and
·0371 „ H_2O.

III. ·3152 grm. of substance gave
·4093 „ CO_2, and
·0409 „ H_2O.
IV. ·3292 „ substance gave
·4319 „ CO_2, and
·0445 „ H_2O.

These numbers give percentages agreeing with the formula—

$$C_9H_4Br_2O_2,$$

as the following comparisons will show :—

	Theory.		Experiment.			
			I.	II.	III.	IV.
C_9 ..	108	35·53	—	35·83	35·41	35·78
H_4 ..	4	1·31	—	1·44	1·44	1·50
Br_2..	160	52·63	52·97	—	—	—
O_2 ..	32	10·53	—	—	—	—
	304	100·00				

This substance is, therefore, coumarin with two of hydrogen replaced by bromine, and may be called *dibromocoumarin*.

Dibromocoumarin fuses at 174° C., and distils nearly unchanged. It dissolves easily in boiling alcohol, and crystallises from this solvent in small needles.

The mother-liquors from dibromocoumarin contain more or less of a second substance, which may be obtained by evaporating off part of the spirit, and recrystallising the product, which separates out several times. This body is not easily obtained in quantity. On analysis it gave the following results :—

I. ·1905 grm. of substance gave
·1579 „ AgBr.
II. ·2548 „ substance gave
·4506 „ Co_2 and
·0504 „ H_2O.
III. ·2271 „ substance gave
·3975 „ Co_2 and
·0471 „ H_2O.

These numbers give percentages agreeing with the formula—

$$C_9H_5BrO_2,$$

as the following comparisons will show :—

	Theory.		Experiment.		
			I.	II.	III.
C_9	108	48·00	—	48·23	47·74
H_5	5	2·22	—	2·20	2·30
Br	80	35·56	35·27	—	—
O_2	32	14·22	—	—	—
	225	100·00			

This body is therefore coumarin with one of hydrogen replaced by bromine, or *bromocoumarin*.

Bromocoumarin melts at 110° C. It is more easily soluble in spirit than dibromocoumarin. It crystallises in transparent prisms, which are often beautifully curved.

When heated with potassic hydrate, both bromo- and dibromocoumarin dissolve, forming a yellowish solution, and on boiling for a short time, crystalline products are obtained. These consist of the potassium salts of new acids, which may perhaps be brominated coumaric acids. These are at present under examination.

It may be worth remarking that the dibromide of coumarin possesses the same composition as mellilotic anhydride with two of hydrogen replaced by bromine, thus:—

$C_9H_6O_2Br_2$. Dibromide of coumarin. $C_9H_6Br_2O_2$. Dibromomellilotic anhydride.

I do not think, however, that they will be found to be identical.

XXX.—*On Organic Matter in Water.*

By Charles Heisch, Lecturer on Chemistry at the Middlesex Hospital Medical College.

In common with most chemists, I have for many years directed my attention to this subject, and in common with many I have long since come to the conclusion that the mere *quantity* of organic matter, nitrogenized or not, forms a very poor basis on which to found an opinion as to the wholesome character of

any sample of water. Believing, as I do, that the deleterious nature of organic matter is dependent on its containing living germs, which grow and set up a fermentative action within the body, I feel convinced that if only a few of such germs be swallowed, they may increase, under proper conditions, to a number to be injurious, and that therefore their original number is a matter of comparatively small importance. My attention has therefore been directed principally to discovering the presence of such germs, and determining their characteristic properties and appearance. I was first led to a means of doing this by being called on to assist a large manufacturer of lemonade, who some years ago almost suddenly found it impossible to make lemonade that would keep. After a day or two it became turbid, and its odour anything but agreeable. On examining the liquid under the microscope, I found it full of small spherical cells, with, in most cases, a very bright nucleus, and after a few days the odour of butyric acid was unmistakable. After examining all the materials employed, I found that the water was in fault. On putting a few grains of the purest crystalline sugar I could procure into some of the water, it became turbid in a few hours, and the same cells were distinctly to be seen with an $\frac{1}{8}$ inch object glass; but the butyric odour did not come on for some days. This water was procured from a deepish well; it was hard, and contained a considerable amount of nitrates, but not any unusual quantity of ammonia or unoxidized organic matter. On inquiry, I found some digging had been going on near the well, and it appeared that some drainage must have got in, though at the moment so small in amount as to be hardly appreciable. When water from the waterworks was substituted, every thing got right again. This led me to try all the samples of water I could procure, in the same manner; and in every case where diarrhœa or other mischief could with any kind of certainty be traced to the use of a certain water, when that water was treated with sugar, these same cells made their appearance, usually within 24 hours, if the temperature were kept up to between 60° and 70°, and plenty of light admitted to the bottle in which the sample was contained. Pressure of other business prevented my making all the experiments I wished on this subject until within the last year, when I have been trying what substances contain these particular germs, which are so

peculiar as to be quite unmistakable when the observer is once familiar with them. By permitting the action of these germs on sugar to go on, they present uniformly the following appearances. The cells gradually group together in bunches something like grapes, quite differently from the ordinary yeast globules; they next spread out into strings, with a wall surrounding and connecting the cells; the original cell-walls then seem to break, and leave apparently tubular sort of threads branched together. The strong resemblance of these to, if not identity with, the sewage fungus, coupled with the almost universal properties of water which produced them, led me to look to sewage as their source, and I found that the smallest quantity of sewage mixed with a water which might be treated with sugar, and remain clear and sweet for weeks, at once produced these germs, or rather set them growing. Water was procured from various sewers, and after standing a few days to settle, six drops of clear water were mixed with 10,000 grs. of West Middlesex and New River water. To 6 ozs. of this mixture 10 grs. of pure sugar were added, a like quantity being mixed with 6 ozs. of the water without the sewage. All these samples were placed in stoppered bottles in a window, where plenty of light could reach them. The water and sugar remained clear and sweet. The water with this trace of sewage did the same. The water, sewage, and sugar became turbid, in times varying from 24 to 60 hours, and exhibited the cells and strings before spoken of, and ultimately the odour of butyric acid was always perceptible. One drop of fresh urine in 10,000 grs. of water, a mixture which may be kept for weeks without showing any sign of turbidity, produced in 24 hours abundance of cells, and in 48 hours branched strings. No other substances which I have tried produce the same result. Urea, albumen, nitrates, milk, and various other things have been tried, and though some have produced growths of some sort, none have resembled these peculiar and unmistakable cells and strings. A curious circumstance took place during the last outbreak of cholera in 1866. On some few days the water of one of the water companies, which is ordinarily perfectly without action on sugar, produced, to a slight extent, those same growths, on being mixed with that body. The appearance of the butyric odour appears to be a question of quantity or time. If a water contain a large number of those cells, it may make its appearance in 24 hours;

sometimes not for a much longer time; but, sooner or later, I believe it is always an accompaniment of these growths. Filtering the water through the finest Swedish paper does not remove the germs, as on the addition of sugar they grow as fast as ever. Boiling for half an hour in no way destroys their vitality. Filtration through a good bed of animal charcoal is, as far as I can find at present, effectual in removing them, and if the charcoal be well aired from time to time, it retains its power for several months; but if the water be passed continually through it without this precaution, it soon loses it, and the filtered water is as bad as the unfiltered. I am now engaged in a series of experiments to ascertain what substances, if any, retard or prevent the growth of these germs; but at present I feel certain only of this fact—that the softer the water, the more quickly they grow. In hard water their first appearance is also not a mere turbidity, but they seem to form in small clots, which on examination are found to consist of the cells mixed with crystals of carbonate of lime. The addition of nitrates or ammoniacal salts to the water, does not seem to accelerate the growth of the cells. With the view of ascertaining how far the presence of the amount of sewage which could be traced by the formation of these growths would be indicated by other means, samples of the water experimented on were submitted, before and after the addition of the sewage, to examination, by the method of Messrs. Wanklyn and Chapman, with the following results:—

New River water.

Ammonia	0·0022 grs.	in gallon.
Organic ditto	0·0047 grs.	„

New River water with six drops of sewer water in 10,000 grs.

Ammonia	0·0027 grs.	in gallon.
Organic ditto	0·0061 grs.	„

Another sample gave—

Water alone.

Ammonia	0·000 grs.	in gallon.
Organic ditto	0·0031 grs.	„

Water with same amount of sewage.

Ammonia	0·0056 grs.	in gallon.
Organic ditto	0·0050 grs.	„

Although this shows an increase, yet the amount was in neither case such as to make one suspect mischief from the water. I am by no means prepared to say that these germs are the only unwholesome kind of organic matter that exists in water, or that water containing small numbers of them might not sometimes be taken with impunity; but I should always look with great suspicion on any water in which they existed, even in the smallest number, as they increase and multiply with great rapidity; and the fact that in multitudes of cases which have come under my notice within the last few years, a great increase of health and comfort has resulted from giving up the use of water in which they could be found, even where its use had not produced positive disease, confirms me in this opinion. Whether these cells are the true butyric ferment I cannot at present say for certain, but I am strongly inclined to that opinion, and I feel quite convinced that when they occur in water they are distinct evidence of sewage contamination.

XXXI.—*On the Methods for the Determination of Carbon in Steel.*

By W. D. Herman, Student at the Royal College of Chemistry.

Whilst studying the process for determining carbon in steel, known as Eggertz's colorimetric method, I observed certain irregularities and imperfections in its practical working which induced me to investigate this method of analysis more closely, and to submit it to a series of comparative experiments which I trust will help to clear up the doubts that many besides myself have entertained, and that the results which I now submit to the Society in a somewhat condensed form may be deemed acceptable.

One of the most serious difficulties of Eggertz's process, arising from the instability of the standard coloured liquid employed, viz., a solution of burnt sugar, had been overcome for some time past by Mr. Valentin, who employed with

perfect success a solution of sulphindigotic acid, which had undergone decomposition by exposure to sunlight. A portion which had been sealed up in July, 1868, has remained quite stable ever since. Samples of the same indigo solution have been in use with equal success at Mr. Siemens' steel works, and at several steel works at Sheffield.

Although much was gained by substituting a stable colorimetrical standard for an instable solution, it was still apparent that the colour of the solution of various samples of steel in nitric acid, especially of those containing larger quantities of carbon, did not always coincide in tint with the new colour standard. I found that a solution of dipotassic dichromate, mixed with more or less of a solution of cobaltous nitrate, was more manageable when different tints of steel solutions had to be matched, although the colour of a column of the solution, when viewed from above, appears invariably yellow, and quite unlike that of the steel or indigo solution. I also had some difficulty in determining the amount of carbon in harder kinds of steel by Eggertz's colour test, and as the differently tinted solutions were mostly obtained when steels containing higher percentages of carbon were dissolved in nitric acid, and then diluted to the strength of the standard solution (= ·5 per cent. of carbon), I was naturally led to suspect that the rate of dilution might possibly not be attended by a proportionate change in the shade of colour of the standard liquid, and I therefore determined upon corroborating the colorimetric results by other methods of analysis.

There was one method in particular that presented itself most temptingly—a process described in the fifth edition of "Fresenius' Quantitative Analysis" as "A. H. Elliott's method," and of which the following is an outline:—

"From 2 to 2·5 grms. of iron in a moderately fine state of division are dissolved, with the aid of a gentle heat, in a solution of cupric sulphate. The precipitated copper is removed by means of hydrochloric acid and cupric chloride, and the separated carbon collected on an asbestos filter, washed free from chlorides, and transferred to a flask, where it is to be heated with a mixture of sulphuric and chromic acids. The carbonic anhydride resulting from the oxidation is dried and then absorbed in a U-tube filled with soda-lime. When gas ceases to be evolved the flask is allowed to cool, and all the

carbonic anhydride in the apparatus driven into the soda-lime tube by a slow current of pure dry air."

Now the only points in which this method differs from that of Ullgren, described in "Fresenius' Quantitative Analysis," 4th edition, p. 660, are—

1st. The removal of the apparatus for condensing the acid vapours arising from the mixture in which the carbon is heated.

2nd. That instead of decanting off the solution of ferrous sulphate formed by the action of cupric sulphate upon the iron, and treating the residue at once with chromic and sulphuric acids, Mr. Elliott prefers to remove the copper with hydrochloric acid and cupric chloride, and to filter off the carbon through asbestos.

By this he introduces an additional complication into the process, for the filtration and washing out of the chlorides require from two hours to two days, according to the amount of carbon present. Although the solution at first filters tolerably rapidly, yet when once a layer of carbon is deposited upon the asbestos, the liquid almost refuses to pass through; besides this there is the risk of losing some of the carbon by this method of filtration. I found that a considerable amount of washing might be dispensed with by causing the gases evolved by the action of the sulphuric and chromic acids to pass through a small U-tube, filled with fragments of glass moistened with a solution of argentic nitrate, before entering the drying tubes.

In determining the carbon in four samples of steel* by this method, I obtained the following figures:—

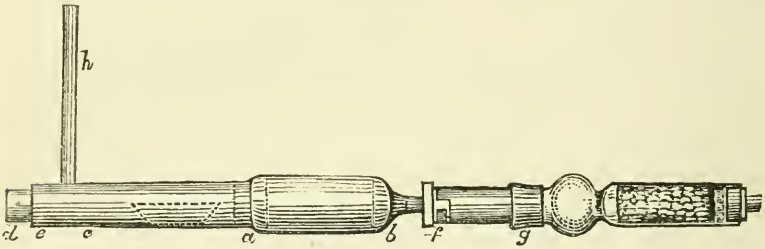
Sample.	VII.	IV.	III.	A.
1st Experiment	·903	·451	·421	·9422
2nd „	·7824	·554	·533	·9433
3rd „	·734			

Although accurate results can be obtained by Ullgren's method, or Elliott's modification of it, I found the process nevertheless tedious, requiring great care and constant atten-

* I am indebted to Mr. R. Smith, of the Porter Steel Works, Sheffield, for the eight samples of crucible steel employed in these experiments.

tion. Since the most direct methods of analysis are known to be the best, I resolved upon burning the iron or steel at once in a stream of oxygen,—a method of combustion first proposed, I believe, by Wöhler. The heat produced by burning iron in oxygen is of course very great, and the best combustion glass frequently cracked on cooling. This difficulty was overcome by using a platinum-tube, represented in Fig. 1, which Mr. Valentin kindly placed at my disposal, he having used it for the determination of sulphur in coal-gas. I was thus saved from the annoyance caused by the fusing or cracking of glass or porcelain tubes, and was enabled to perform combustion after combustion with the greatest ease.

Fig. 1.



The wider part of the tube between *a* and *b*, which is four inches long, is filled with granulated cupric oxide, prepared by igniting copper wire in a current of air. At *a* and *b* are two small asbestos plugs to retain the oxide in its place. The portion between *c* and *a* is destined to receive the boat—platinum or porcelain—containing the substance to be burnt, after the introduction of which the open end of the tube is closed by a cork *d*, kept cool by the application of a wet rag to the outside at *e*. A bronze tube, tinned inside, is connected with the platinum tube by means of a bayonet joint *f*, and at *g* with a small glass tube containing plumbic dioxide, to which a drying tube and potash-bulbs are connected in the usual way. The oxygen is delivered through *h*. The combustion is conducted in the ordinary way, only that the tube must be heated in a Griffin's gas-combustion furnace.*

An experiment was first tried with pure sugar to ascertain

* It need scarcely be remarked that a tube adapted for combustions generally, and not for the special purpose of determining sulphur in coal-gas, could be constructed in a much simpler manner.

whether a stream of oxygen in conjunction with a layer of only four inches of cupric oxide, would be sufficient to convert all the carbon into carbonic anhydride. The result was perfectly satisfactory, an amount of carbonic anhydride being obtained equal to 42·086 per cent. of carbon instead of 42·105, showing a loss of only ·019 per cent. upon the theoretical amount.

The platinum tube was next applied to the combustion of the washed and dried carbonaceous residue obtained by Elliott's method. An ordinary glass combustion-tube would answer the purpose nearly as well, since the heat required for the combustion of this residue is not so very intense. The results were good, although some slight loss was occasioned by the transfer from the funnel to the boat.

In determining carbon in steel by direct combustion, I proceeded as follows:—The steel previously softened was reduced to fine filings by means of a *single-cut* file. The advantages derived from the use of a single-cut file are twofold; 1st, the danger of breaking off the teeth is reduced to a minimum, and 2ndly, the filings produced are in fine shreds, a condition very favourable to rapid and complete oxidation. A quantity of filings varying from 1 to 2½ grammes, according to the percentage of carbon, was weighed out into a small platinum-boat, and introduced into the platinum tube, the anterior part of which containing the cupric oxide had been previously heated to redness. All the taps underneath the part of the tube containing the boat with the filings, may be turned on at once, as there is no fear of any sudden rush of carbonic anhydride. A moderately quick current of oxygen, prepared from potassic chlorate, and purified and dried by passing first through a solution of argentic nitrate, then through a solution of potassic hydrate, and finally through tubes filled with fragments of coarsely-pounded glass moistened with concentrated sulphuric acid, was then transmitted through the tube. The carbonic anhydride resulting from the combustion of the carbon in the steel, together with the excess of oxygen, was made to pass through a small tube filled with plumbic dioxide, in order to arrest any traces of sulphurous anhydride formed by the oxidation of sulphur, and through a calcic chloride tube, before reaching the potash-bulbs. These latter were fitted with a small guard-tube, filled with fragments of caustic potash, to

arrest the moisture carried off from the potash solution by the excess of dry oxygen.

The time required for complete combustion depends upon the quantity and state of aggregation of the steel employed, and upon the temperature. The oxidation of 2 grms. of steel was usually accomplished in forty minutes. If the filings are placed in a platinum-boat, it is advisable not to raise the temperature too high, nor to pass the oxygen too rapidly, since the heat generated by the combustion of the iron in oxygen is so intense as to fuse the ferric oxide, and thus to endanger the boat. By employing a moderate heat no such accident need be feared. The oxide obtained, having invariably the composition of Fe_2O_3, could readily be removed from the boat in the form of a semi-fused, non-magnetic mass. Its composition proved so constant, that it actually formed the criterion for a complete or incomplete combustion. Thus whenever, on weighing, the residue did not agree in composition with the formula Fe_2O_3, I invariably placed the boat again into the combustion tube.

The concordance of the amount of oxide found by experiment with that deduced by theory, as well as the constancy in the percentage of carbon, will be seen from the following experiments:—

Sample of steel, No. VII.	Quantity of steel employed for combustion.	Percentage of carbon found.	Fe_2O_3 found.	Calculated amount of Fe_2O_3.
Experiment 1	1·3935	·7632	1·9765	1·9755
„ 2	1·58105	·7590	2·2423	2·2415
„ 3	1·2045	·7585	1·706	1·707

The method of procedure recommended by Eggertz, as best adapted for obtaining accurate results by his colour test, may be summarized as follows:—About ·1 grm. of the steel is to be treated with from 1 to 5 c.c. of nitric acid, sp. gr., 1·2. When the steel is dissolved, the solution is heated to 80° C., and kept at this temperature until gas ceases to be evolved. This usually requires from two to three hours. The liquid is then diluted, until it coincides in tint with a standard steel solution, containing ·0001 of carbon to the cubic centimetre.

I have varied the details of the method in different ways,

and find that the original process cannot be departed from without affecting the accuracy of the results. The effect, for instance, of prolonged digestion at 80° C., or the action of a boiling temperature for a short time, is markedly shown by the following experiments upon Sample A :—

By combustion obtained in two experiments						·921 per cent. C. ·922 „
By digesting at 80° for about			3 hours			·931 „
„	„	80°	„	15 „		·492 „ ·477 „ ·455 „
„	„	100°	„	2 „		·660 „ ·714 „

The causes of such errors may of course be readily avoided, but a difficulty that is not so easily overcome, arises from the fact that samples of one and the same steel, treated under apparently the same circumstances, and diluted to the same extent, give differently coloured solutions, either greenish, reddish, or yellowish; at one time resembling in tint the indigo solution, at another approximating more closely to the mixture of dipotassic dichromate and cobaltous nitrate, and occasionally differing from both. Steels also containing different percentages of carbon, when diluted to the standard strength (*i.e.*, so that each c.c. should contain ·0001 of carbon), seldom yield solutions of the same colour. Thus in two steels containing say 1·0 and 0·25 per cent. carbon respectively, it will generally be found that the one containing the larger percentage of carbon, on dilution to the standard strength, yields a solution with a pinkish tinge, whilst the steel, containing only ·25 per cent., affords a green one. An approximation to the truth in such a case may be obtained by paying not so much attention to the tint of the solution as to the *depth* of its colour. A better plan, however, is to prepare several standards, each indicative of ·0001 of carbon per c.c., but differing in their tints. This may readily be done by dissolving, according to Eggertz's directions, known quantities of steels containing different proportions of carbon (the percentages of which had been previously accurately determined by combustion), and diluting each solution to the standard strength. The solutions thus obtained cannot be employed as standards directly, since they speedily lose their colour, even when sealed up. Their colours must therefore be imitated by some stable body, such as the decomposed indigo solution, or mixture of cobaltous nitrate and dipotassic dichro-

mate. For matching the colour of steels containing low percentages of carbon, the indigo solution is invaluable, but for the more highly carburetted steels, I prefer the mixture of the two salts. It is obviously necessary that the steel solutions and the coloured standard liquid should be in tubes of the same diameter. In my experiments I employed ordinary test-tubes, half-inch in diameter, and about 5 inches long, graduated into cubic centimetres.

The following figures were obtained by working most carefully, according to Eggertz's directions:—

Steel from Crewe.	VIII.	VII.	VI.	V.	IV.	III.	O.
1·440	1·367	·810	·743	·645	·492	·330	·267
1·239	1·212	·635	·827	·670	·558	·365	·318
	1·515	·898	·713	·547	·484	·340	·272
	1·160	·846	·611	·588	·525	·360	·276
	1·692	·921	·496	·515	·410		
	1·135	·625	·676	·560	·451		
	1·151		·844				
Mean 1·339	1·319	·789	·701	·587	·486	·349	·283

The following Table contains a *résumé* of some of the results obtained by the four different methods which I employed for determining the carbon in the samples of steel:—

	VIII.	VII.	VI.	V.	IV.	III.	O.	A.
By chromic acid method	1·248	·903 ·7824 ·734	·724	·6701	·451 ·554	·4214 ·533	·349	·9433 ·9422
By direct combustion of filings in oxygen	1·1802 1·1510	·7632 ·759 ·7584	·649 ·620			·3596 ·3592	·273	·921 ·922
By combustion of carbon, separated by dissolving the steel in SO_2Cuo.	1·165	·7086						
By colour test. Mean from previous table	1·319	·789	.701	·587	·486	·349	·283	

To sum up briefly.

1st. It would seem from these experiments that Eggertz's process cannot be employed when the amount of carbon is large, and is required to be known with accuracy.

2nd. The method of combustion in oxygen is preferable, as being direct, expeditious, and capable of giving accurate results.

3rd. The completion of the combustion can be readily ascertained, whereas in the processes for combustion hitherto employed, this point is always left in doubt.

I beg to express my best thanks to Mr. Valentin, for the valuable advice he has given me in conducting these experiments.

XXXII.—*On the Determination of Phosphoric Acid.*

By William Carleton Williams, Student in the Laboratory of Owens College.

[From the Proceedings of the Manchester Literary and Philosophical Society.]

Of the many methods proposed for the separation of phosphoric acid from the alkaline earths, few are better than the one devised by W. Reissig, founded upon a process originally described by Reynoso. This method, although used in many German laboratories, has, strange to say, found but little favour among English chemists. This is probably owing to the somewhat complicated and tedious nature of the operations required. The modifications described in the following communication considerably simplify the process, and may possibly lead to its more general adoption.

Reisig's method depends upon the fact that, when metallic tin is added in excess to a solution of the phosphate of the alkaline earths in nitric acid, the stannic acid formed by the oxidation of the metal combines with the phosphoric acid and completely removes it from solution. On filtering, therefore, we at once separate the alkaline earths which remain in solution from the insoluble combination of stannic and phosphoric acids. In order to determine the amount of phosphoric acid

contained in the tin oxide, the compound is dissolved in a small quantity of concentrated potash solution, when the two acids dissolve as meta-stannate and phosphate of potassium; the fluid is now saturated with hydrogen sulphide, a small quantity of ammonium pentasulphide is added, and, lastly, a slight excess of acetic acid. The tin sulphide is then separated by filtration: all the phosphoric acid is contained in the filtrate, and its amount may be determined by the ordinary method as magnesium ammonium phosphate.

The chief disadvantage of this method arises from the necessity of employing a large excess of metallic tin, in order to completely remove the phosphoric acid from solution. The bulk of tin sulphide obtained is therefore very large, and its filtration and washing is an exceedingly long and tedious operation. In order to shorten the process, Reissig recommends that the alkaline solution of the phosphate and stannate be transferred to a weighed flask of 1000 cubic centimetres' capacity, and then diluted with water until the fluid measures about 900 cubic centimetres; the solution is next saturated with hydrogen sulphide, then ammonium sulphide and acetic acid in slight excess added, and the mixture diluted until the whole weighs 1000 grms. After standing for a few hours the clear supernatant liquid is carefully poured through a filter, taking care not to disturb the precipitate. In the filtrate the phosphoric acid is estimated as magnesium pyrophosphate. The amount of the fluid employed in the determination is ascertained by again weighing the flask. On subtracting the weight of the tin sulphide calculated from the quantity of the metal originally employed, we have all the data required to determine the amount of phosphoric acid in the entire solution.

This method of proceeding is not altogether faultless in principle. (1.) It presupposes that from a known weight of tinfoil we are able to calculate the amount of tin-sulphide it will yield. Now the tinfoil of commerce is seldom or never pure; it almost invariably contains a considerable proportion of lead, often amounting to one-third of its weight,* and this of course passes into the nitric acid solution of the alkaline earths. (2.) Since only a portion of the phosphoric acid present is actually

* The tinfoil employed in my experiments contained 31·35 per cent. lead.

weighed, the remainder being deduced by calculation, the chances of ultimate error are considerably increased.

These sources of error are removed by simply filtering and washing the tin sulphide by means of the Bunsen "water-pump," an operation of comparatively short duration. We thus obtain the whole quantity of phosphoric acid in solution, and entirely obviate the numerous weighings, involving, too, the very uncertain correction for the amount of tin sulphide present.

In order to test the trustworthiness of the method thus modified, the following experiments were undertaken. A quantity of pure calcium phosphate was prepared by adding calcium chloride to an excess of sodium phosphate, and the precipitate washed, dried, and ignited. About 0·5 grm. of this compound was weighed out into a porcelain basin, and dissolved in a small quantity of nitric acid: the solution was then concentrated, and the strongest nitric acid (boiling at 86° C.) added until the calcium nitrate commenced to separate out. This was immediately redissolved by the addition of a few drops of dilute nitric acid. The nitric acid solution is now in the highest possible state of concentration: on throwing a small quantity of tin into this solution, the metal is rapidly oxidized to stannic acid, and the supernatant liquid remains perfectly clear. The preliminary heating of the solution is indispensable, since in the cold the metal is apt to become passive, when it completely resists the action of the acid. The precipitate is now dissolved in a small quantity of caustic potash, and saturated with hydrogen sulphide: on adding acetic acid in slight excess the tin sulphide is precipitated. The precipitate is then separated by means of the Bunsen "filter-pump," and the whole of the phosphoric acid is contained in the filtrate. After concentrating the solution, and again filtering from a minute precipitate of tin sulphide, which invariably separates out (tin sulphide being slightly soluble in solutions containing hydrogen sulphide), the phosphoric acid may be precipitated as the magnesium-ammonium salt, and weighed as pyrophosphate—

I. Ratio of tin to phosphoric acid, 4 to 1.

1. 0·5135 grm. cal. phos. gave 0·405 $Mg_2P_2O_7$ = 50·45 % P_2O_5
2. 0·447 „ „ 0·358 „ 50·78 „

Mean..... 50·61 % P_2O_5

The lime was determined as caustic lime after removal of the lead by means of hydrogen sulphide. The mean of two concordant analyses gave 49·65 per cent. lime.

Hence the composition of the calcium phosphate is, phosphoric acid 50·61, and lime 49·65 per cent.

It is therefore evident that the amount of pure tin required need not exceed 4 times the weight of phosphoric acid present.

The following experiments show that this is moreover the minimum quantity that can be used:—

II. Ratio of tin to phosphoric acid = 3·0 to 1.

0·477 grm. cal. phos. gave 0·307 $Mg_2P_2O_7$ = 41·53 per cent. P_2O_5.

III. Ratio of tin to phosphoric acid = 3·5 to 1.

0·598 grm. cal. phos. gave 0·388 $Mg_2P_2O_7$ = 41·5 per cent. P_2O_5.

0·434 grm. cal. phos. gave 0·304 $Mg_2P_2O_7$ = 44·82 per cent. P_2O_5.

In order to confirm the above results, I have determined the proportion of lime and phosphoric acid contained in the calcium phosphate employed in the analyses, by dissolving the compound in hydrochloric acid, and adding sufficient sulphuric acid to precipitate the base. To each volume of the liquid two volumes of alcohol were added, and the mixture allowed to stand about 12 hours, when it was filtered and the precipitate thoroughly washed with alcohol. The filtrate containing the phosphoric acid is evaporated to dryness, the residue dissolved in water, and the acid precipitated as the magnesium ammonium salt. The lime was weighed as sulphate—

I. 0·525 grm. gave 0·411 Mg. P_2O_7 = 50·08 per cent. P_2O_5.
II. 0·507 „ 0·396 „ „ = 49·96 per cent. P_2O_5.

The lime amounted to 50 per cent. Hence the composition of the calcium phosphate is 50·02 P_2O_5 and 50·00 CaO, exactly agreeing with the determinations made by the tin method.

XXXIII.—*On Fungi and Fermentation.*

By James Bell, F.C.S., &c.

A series of experiments has been instituted, and is still in progress, to determine the forms of natural ferment which albumen and other nitrogenized substances give rise to.

Albumen and Gluten.—The albumen of egg was first selected for experiment. To a solution of cane sugar a small quantity of egg albumen was added, and the sample was placed in a chamber which was kept at a temperature of 75° Fahr.

In a few days numerous minute transparent cells or spores, with a bright nucleus, were found to be diffused throughout the liquid; these soon increased in size, but the largest were relatively much smaller than the cells of wort or wine ferment. The sample was examined on several occasions for alcohol, but great difficulty was experienced in the distillation on account of the frothing caused by the presence of the albumen. The largest quantity of alcohol* found in the liquid at any one time amounted to only about two-tenths per cent.

The liquid gradually became acid, and in two or three weeks was found to be full of *vibrios*. At the end of 46 and 74 days respectively, the sample contained 1·02 and 2·16 per cent. of acid, and on the latter occasion it contained no alcohol whatever, the acidifying power having become greater than the alcoholic.

Gluten was next selected for experiment. A sample was carefully prepared from wheat flour, and a portion was introduced into a cane sugar solution. The gluten at first floated on the surface of the liquid, but in a few days it became much disintegrated and subsided to the bottom of the flask, and afterwards became gradually diffused throughout the liquid.

In a few days small transparent cells were seen to be tolerably abundant in the liquid, but they did not appear to produce much action. The sample was frequently examined for alcohol, but very little was found to have been produced; and at the end of 34 days it only contained 1·65 per cent. of alcohol and ·24 per cent. of acid.

* The alcohol in each case is given as absolute, and the percentage is estimated by volume.

The spores or cells in this case had a bright nucleus similar to that which characterized the egg albumen cells.

Wheat flour albumen was next tried, and in the first instance a cold-water extract was prepared, the starch and other insoluble constituents being separated by filtration. The clear filtrate containing the albumen in solution was divided into two portions; to one 21 per cent. of glucose was added, and to the other about 15 per cent. of cane sugar.

In a day or two after the samples had been prepared they were both found to be full of microscopic parasites, and the one containing the cane sugar soon became thick and syrupy, the sugar having been converted into mucilage.

At the expiration of 24 days, the sample to which the cane sugar had been added was examined for alcohol and acid, and was found to contain six-tenths per cent. of acid,* but no alcohol.

The portion of the extract to which glucose had been added became turbid and slightly mucilaginous; and at the expiration of 24 days the sample was examined for alcohol and acid, and was found to contain ·72 per cent. of acid, but only 0·17 per cent. of alcohol. There were present a few cells resembling those of yeast, but they appeared unhealthy and inactive.

From these results it was obvious that in order to study the ferment which albumen derived from wheat flour would give rise to, the albumen would have to be prepared in a pure form, and introduced directly into the sugar solution.

A small quantity was therefore prepared by heating a cold-water flour extract, and separating the coagulated albumen by filtration. The albumen after having been well washed was introduced into a solution containing 15·62 per cent. of glucose, and the sample remained free from microscopic parasites for upwards of a week, although the air had access to the liquor through a glass tube.

At the end of 14 days the sample was examined for alcohol and acid, and was found to contain neither. In the meantime mycelium was observed developing throughout the albumen, and giving rise to transparent spores or cells with a bright nucleus similar to those which occurred in the egg albumen sugar solution.

* The acid is estimated as acetic.

The sample was again examined for alcohol at the end of a month, and was then found to contain one-tenth per cent.

Another small quantity of albumen was prepared from wheat flour, by precipitating the albumen from the cold-water extract by alcohol. The precipitated albumen was then diffused through water, which was afterwards heated for some time to drive off the alcohol, and about 15 per cent. of glucose was added to the albuminous liquid. On the following day, however, the sample was found to contain a considerable number of the microscopic parasites, which it was intended to get rid of; in fact, a large proportion of the germs present in the flour extract was enclosed in and carried down with the precipitate.

At the end of 14 days the sample was examined for alcohol and acid, and was found to contain ·12 per cent. of acid, but no alcohol. Now it will be observed that the result in this case is different from that obtained in the experiment with the albumen which had been prepared by coagulation; in the one case there were microscopic parasites present, while in the other they were absent.

This sample was again examined for alcohol at the end of 28 days, when it was found to contain ·19 per cent.

In this experiment, the mycelium developed in the albumen was similar to that formed in the albumen prepared by coagulation.

Albumen was prepared from ground malt in exactly the same manner as in the case of the flour, and the like experiments were performed with it in sugar solutions with almost identical results. The albumen prepared from the malt extract by heating was also found to be entirely free from microscopic parasites, while that obtained by precipitation abounded with them. Some yeast cells, however, as might be expected, were found in the sample to which the malt albumen that had been precipitated by alcohol was added, and the solution contained a larger percentage of alcohol than any other of the albuminous samples.

The experiments in the case of the malt were carried a little further. The alcohol contained in the malt extract from which the albumen had been precipitated, was removed by distillation, and to the residue about 15 per cent. of cane sugar was added. On the fourth day fermentation set in, and the ferment produced was the purest and finest specimen that I have seen, and the sample was entirely free from microscopic parasites.

In fact, the germs which escaped being carried down by the alcoholic precipitate appeared to have been subsequently destroyed by long boiling in distilling off the alcohol. At the end of ten days the sample contained 10·63 per cent. of alcohol, and only ·18 per cent. of acid; so that, after all the manipulations through which the extract was put, the natural ferment produced possessed considerable powers, and which were still unexhausted.

The various germs and organisms infesting grain are the most formidable enemies with which we have to contend in the fermentation of grain extracts. If these once obtain possession of the field, and gain the ascendancy, they materially interfere with the success of the fermentative process.

A temperature of about 175° Fahr., at which grain extracts are usually prepared, is not sufficient to destroy the germs; their vitality may be suspended, but if the subsequent conditions are favourable to their growth, they soon become developed.

To determine the effect which boiling has upon the natural fermentation of a malt extract, a comparative experiment was made. An infusion of malt was prepared and kept for two hours and a half, at a temperature between 170° and 180° Fahr. The extract was then divided into two portions, one of which was boiled for some time, and afterwards about 15 per cent. of glucose was added to each portion. At the end of ten days the portion which had been boiled contained 10·38 per cent. of alcohol and 0·27 per cent. of acid, while the other contained 0·78 per cent. of acid and only 6·26 per cent. of alcohol.

In the one case the yeast cells had possession of the field first, whereas in the other it was simultaneously occupied by a variety of organisms.*

A cold-water extract of barley meal possesses the property of converting cane sugar into mucilage, but yeast cells soon develop, and resolve the greater portion into alcohol and carbonic acid gas. This is a most interesting phenomenon, and serves to convey some idea of the wonderful power and singular properties of the yeast plant.

Under the microscope the yeast cells can be seen in the mucilaginous mass, sometimes in bundles resembling a bunch of

* There has been a considerable difference observed in the number of parasites and germs present in different samples of malt.

grapes, and sometimes in a chain-like form, the multiplication of the cells being apparently carried on by a process of budding.

Cane sugar is not converted into mucilage in all extracts prepared from barley meal. In a great many cases, especially in summer, and under the influence of a high temperature, the yeast cells begin to act soon after the preparation of the extract and counteract the formation of mucilage.

The formation of mucilage is also prevented if, before the addition of the sugar, the extract is boiled for about half an hour in order to destroy the germs and microscopic parasites.

In cold-water extracts of malt, to which cane sugar has been added, the cane sugar is not converted into mucilage. There is at first a slight tendency to thickening, but vinous fermentation soon sets up, which prevents the formation of mucilage.

From malt extracts prepared in the cold, with the addition of sugar, very fair fermentations can be obtained; but as the samples are primarily occupied by a variety of living things, a large percentage of acid is produced, and a considerable loss of alcohol is sustained.

The results hitherto obtained point to the microscopic parasites as being the proximate cause of the transformation of cane sugar into mucilage, and the production of acid.

Moulds and Pus.—A few experiments have been made with certain moulds, and one with pus, to determine their respective actions in sugar solutions.

The study of the development and properties of moulds, like that of most matters connected with fungi, is undoubtedly a critical one, as is fully evidenced by the absence of an agreement of opinion on the subject.

My inquiry has been directed to the action of moulds rather than to determine their origin and mode of development, but as it is alleged by some that the blue mould of malt, &c., is the ultimate development of the yeast plant, I cannot help stating that I have failed in my experiments to identify it as such; on the contrary, the moulds appear to preserve their distinctive character, and to be identified with a more advanced stage of decomposition than the true yeast plant.

It is not improbable that there is some relation subsisting

between the yeast plant and certain of the moulds, but whatever the relation is, it is obviously not yet understood, and remains to be determined.

A quantity of blue mould with the pasty mass attached was collected from the surface of moistened ground malt, and introduced into a sugar solution containing 15 per cent. of glucose, and the sample was placed in a chamber maintained at a temperature of 70° Fahr.

On the third day the liquid was alive with microscopic parasites, and carbonic acid gas was being eliminated. On the fourth day it contained ·18 per cent., and on the sixth day ·28 per cent. of acid, and ·17 per cent. of alcohol. On the ninth day it contained 1·34 per cent. of alcohol and ·42 per cent. of acid; and at the end of twenty-eight days 7·48 per cent. of alcohol and ·60 per cent. of acid.

The liquid was now filtered off, and the residue introduced into a fresh solution of sugar; at the expiration of eighteen days the sample was examined, and found to contain about 2 per cent. of alcohol.

The mould up to this time not only maintained its identity, but continued to propagate in the liquid in a brush- or plume-like form, after the fashion of its aërial fruiting, and the spores were distinguished from yeast cells by a central ring, and by the comparative absence of granular matter.

A quantity of mould from lemon juice was next obtained, and added to a solution containing 14 per cent. of glucose, and placed in the same chamber in which the preceding experiment was conducted. On the sixth day the sample was found to contain 0·91 per cent. of alcohol, and on the twenty-third day 8·44 per cent. of alcohol and ·24 per cent. of acid.

This mould was extremely persistent, and maintained its position on the surface of the liquid throughout the fermentation; while the mould obtained from the malt became in a short time broken up and diffused throughout the sample.

It is worth noting in the case of the lemon-juice mould, and I have remarked the same thing in natural wine fermentations, that the quantity of alcohol produced fully represents the percentage of glucose; whereas in the case of the malt mould the quantity of alcohol produced is less than it ought to be according to the proportion of the glucose.

A sample of pus was next introduced into a solution contain-

ing 7 per cent. of glucose, and the sample was placed in a chamber kept at a temperature of upwards of 70° Fahr. On the seventh day small transparent cells or spores, and flocculent masses of mycelium were observed floating in the liquid, and at the expiration of sixteen days the sample was found to contain 0·65 per cent. of alcohol, and ·06 per cent. of acid; and it is somewhat remarkable how free the sample was from microscopic parasites.

The mycelium and spores produced in the sugar solution containing the pus are almost identical in character with the mycelium and spores produced in the flour and malt albumen sugar solutions respectively.

The like description of fungoid mycelium development is occasionally met with in boiled malt extracts, but in albumen sugar solutions prepared in the way described, it usually occurs in an isolated form.

It is somewhat curious that this fungoid development in albumen sugar solutions should resemble so closely in character the development of the *micrococcus* in Hydrophobia in one of its stages of cultivation by Dr. Hallier.

From these and the other results which I have obtained it would appear that some fungoid developments other than the *torvula* cells tend to produce in sugar solutions alcohol and carbonic acid gas, but the proportion of alcohol produced within a given time differs greatly.

In this lies the great distinction between the yeast plant proper and the various forms of the *penicillium crustaceæ;* the yeast plant usually makes its appearance in three or four days, and sets to work with an extraordinary degree of energy, producing alcohol in great abundance.

There appears to be a kind of localized action with most fungoid growths in sugar solutions, whereas the action of the yeast plant is general, and it is essential that the material upon which the cells depend for nourishment should be in solution.

Malt and Grape Yeast Plants.—Various comparative experiments have been made to determine the relative fermentative properties of the yeast plants of malt and the grape.

A cane sugar solution capable of yielding 17·5 per cent. of alcohol was prepared, and brewers' pressed yeast was then added in the proportion of 2,000 grains to the half-gallon, and

at different stages of the fermentation fresh quantities of yeast were added. On the ninth day the sample contained 12·32 per cent. of alcohol; on the twelfth 14·15; on the sixteenth 15·57; and on the nineteenth day 15·79, and at the end of thirty-six days 15·91.

It will be seen that during the first nine days alcohol was produced at a rate over 1 per cent. each day, but that its production from that time was extremely slow, and that practically on the sixteenth day, when the sample contained 15·57 per cent., the vitality of the yeast cells was suspended.

When the extreme point is nearly reached the cells become contracted, but when transferred to a fresh sugar solution and placed in favourable conditions, they soon recover and begin to work afresh with their usual vigour. In this and the other experiments every precaution was taken to guard against loss of alcohol by diffusion, as it was found that when about 12 per cent. of alcohol was reached the loss of alcohol in an open vessel was equal to the quantity generated.

Several malt extracts were prepared and the saccharine values thereof were raised to certain points by the addition of glucose, and allowed to ferment naturally.

The malt extracts were prepared by infusion at a temperature of about 170° Fahr., and from what has been already stated I need hardly refer to the difficulty which was experienced in obtaining a pure healthy fermentation from a malt extract prepared at this temperature, although the infusion was maintained at that temperature for upwards of three hours, and the subsequent addition of 30 per cent. of glucose operated as an antiseptic.

The most successful malt wort fermentation was one in which the glucose, including that naturally present in the malt extract, amounted to over 36 per cent., and the fermentation was conducted at a temperature ranging from 63° to 70° Fahr. No fermentation was visible until the sixth day, when a number of hazy cells, which indicate the commencement of fermentation, made their appearance. Soon after this the fermentation began to be brisk, and by the ninth day 10·96 per cent. of alcohol had been generated, or within 1·35 per cent. of the quantity produced in the same time in the cane sugar solution by the addition of yeast. Now, this fact is very interesting, as it serves to show the great facility with which glucose, as com-

pared with cane sugar, is resolved into alcohol and carbonic acid gas, and to indicate the large additional expenditure of force required to effect the two transformations of cane sugar by the fermentative process.

From the ninth day the fermentation began to abate; in the three days following 2·83 per cent. of alcohol was produced, and in the next sixteen days 2·60, making altogether 16·35 per cent. of alcohol, which is the highest amount that has been reached in the fermentation of malt extracts prepared in the way described. It should be noted, however, that in this case the fermented liquid contained over 7 per cent. of glucose, and that it is probable if the proportion of glucose had been less a higher percentage of alcohol might have been produced.

From a series of experiments it has been found that alcohol and sugar combine to act as an antiseptic, and that by increasing the percentage of sugar the fermentative power of the liquid is proportionately decreased. It is upon this property of their combined action that a less quantity of proof spirit is required to be present in liqueur than in ordinary wines, to prevent their deterioration. For example, a properly-made liqueur wine, containing 20 per cent. of glucose and about 14 per cent. of alcohol, would be perfectly safe for keeping, or indeed for removing, to any part of the world; but if the wine contained only 14 per cent. of glucose, to render it proof against deterioration, the proportion of alcohol would require to be increased to about 17 per cent.

The experiments with grape "must" had to be made chiefly with English hot-house grapes, and as these were gathered in the months of December and January, the percentage of glucose was, as might be expected, low; but, as in the case of the malt extract, the percentage was increased to the required point by the addition of pure glucose.

In the fermentation of grape "must" the chief enemy to be encountered is the development of mould spores, which, when once established, affect the flavour of the wine, and in many instances render it unfit for use as a beverage.

As an illustration of this a sample of wine was made from English hot-house grapes, and it would have been a very fair sample considering the conditions under which it was made, were it not that it possessed a musty odour. On the second day after the juice was placed in the chamber for fermentation,

a white mould, *Oidium Tuckeri*, formed on the surface, and attempts were made to remove it, but in vain, as it rapidly diffused itself throughout the juice. On the following day the yeast cells made their appearance in great numbers, and soon took possession of the field, rapidly suppressing the further development of the mould on the surface. It is true the ferment afterwards was never pure, but still the wine yeast cells continued to work until they had produced upwards of 17·68 per cent. of alcohol.

The grape ferment according to my observations is extremely pure and homogeneous in character, and if the conditions are favourable for its growth and development it does its work well. It works with great steadiness and possesses a degree of persistence which does not belong, at least so far as I have seen, to the beer ferment.

In most of the wine fermentation experiments the husks were nearly all fermented with the juice, and everything was adopted which was thought would add to the fermentative power of the "must." In one instance the percentage of glucose was made up to about 36 per cent., and the juice was placed for fermentation in a chamber at a temperature of 65° Fahr. On the fourth day fermentation was visible, and on the tenth day 10·20 per cent. of alcohol had been generated; on the twenty-third day 18·54 per cent.; and at the end of ten days more the percentage had increased to 18·65 per cent., which is the highest point that has been reached in natural wine fermentations. The cells, notwithstanding the amount of work which they had performed, were even at this point bright and globose, and maintained their entirety.

Another sample of juice was similarly treated to the foregoing, but fermented at a temperature 10° higher. The fermentation in this case was visible on the third day, and at the end of 14 days 17·40 per cent. of alcohol had been generated in the "must;" and at the expiration of a month, the temperature being continuously maintained at 75° Fahr., the proportion of alcohol had increased to 18·26 per cent. The yeast cells were much shrivelled, and some appeared to have burst; in fact, altogether the higher temperature was clearly less favourable for good, steady, healthy fermentation.

In another wine experiment the percentage of glucose in the

juice was made up to about 40 per cent., and the fermentation was conducted at a temperature of about 65° Fahr.

The juice was prepared from the same sample of grapes as that employed in the first wine experiment above described, and the two samples were fermented side by side.

The fermentation did not start so soon as in the other wine experiments, the large percentage of glucose having delayed the development of the yeast cells nearly two days beyond the usual time. On the tenth day 10·62 per cent. of alcohol had been generated in the juice, and at the end of a month the percentage of alcohol had increased to 17·26 per cent., being 1·39 per cent. less than the quantity produced in the sample which contained the lower percentage of glucose.

It is upon this and similar results obtained under the like circumstances that the statement above is founded, viz., that the alcohol and sugar combine to act as an antiseptic.

In all these cases the wine ferment has the advantage, and has proved itself to possess greater fermentative powers than the malt ferment.

From the results obtained in the fermentation of grape juice I cannot refrain from expressing my opinion that it would be an improvement in the manufacture of wines if, where the percentage of glucose in grape juice is low, an addition of grape sugar were made before or during the fermentation of the "must."

The addition of the sugar would assist in exhausting the juice of its fermentative element, which is generally in excess of the glucose naturally present, and tend to prevent acetous fermentation, and the development of obnoxious fungoid growths. It would also have the effect of obviating to a great extent the necessity for fortifying many descriptions of wine, and impart to them a greater body by reducing the proportion of water added, and which is present in the alcohol used for fortifying.

In selecting, however, samples of glucose or sugar for this purpose, great care would require to be exercised, to ensure their freedom from microscopic parasites and germs.

The samples of wine which I have prepared appear to be possessed of excellent keeping properties, and to be entirely free from any deteriorating tendency, a result which I attribute to

the exhaustive manner in which the fermentation of the juice was conducted.

In several instances the fermentation in wine juice was started by the addition of brewers' yeast.

The juice was prepared from foreign red grapes, and the percentage of glucose was made up in one instance to 36 and in another to 31 per cent. To each sample, which consisted of about two quarts, 250 grains of brewers' pressed yeast were added, and the fermentation was conducted in a chamber at a temperature of 70° Fahr. On the third day a small quantity of fresh husks of English hot-house grapes with pulpy matter attached was added to each sample, to ensure, as was thought, sufficient fermentative power.

At the end of 14 days the samples contained respectively 13·23 and 15·91 per cent. of alcohol, and at the end of a month the percentages were 13·76 and 15·96, being only an increase during the interval of ·53 in the former case, and ·05 in the latter, so that it was obvious the fermentation in both was completely suspended.

The wine was then carefully drawn off, and a sugar solution was added to each residue, and the flasks were replaced in the fermenting chamber. In a few days a brisk fermentation commenced in both samples, and at the end of a week they contained 7 and 6·5 per cent. of alcohol respectively, thereby showing that the fermentative power was not exhausted, and that the stoppage of the fermentation was due to some other cause.

Now it must be observed that the fermentation had proceeded to a considerable extent before the yeast cells natural to the grape juice had time to develop, and there is no doubt that the alcohol previously generated seriously affected their growth and propagation.

An experiment which was made on another sample will perhaps tend to explain this.

A wine juice made up to 36 per cent. of glucose, and from which the greater part of the husks and pulpy matter had been separated, ceased to ferment when the alcohol had reached 15·97 per cent. With a view of trying to push the fermentation further, a quantity of fresh husks and pulpy matter was added, which had the effect of reducing the proportion of alcohol present to 13·93 per cent. The sample was then successively

tried in a chamber kept at a temperature of 68° and 80° Fahr., but no further fermentation could be induced, a result which would appear to indicate that to obtain a good and an exhaustive fermentation the cells require to develop naturally in the juice, and become gradually acclimatized to the successive changes of conditions produced during the progress of the fermentation.

Effect of Change of Soil.—A few experiments have been made to ascertain the influence of change of soil upon the development of the yeast plant.

To a solution containing 32·24 per cent. of glucose, some albumen of egg, and a small quantity of healthy wine ferment were added, and the sample was placed in a chamber maintained at a temperature of about 67° Fahr.

The wine yeast cells remained bright and healthy, but did not appear to possess much activity; in the course of seven or eight days albumen cells were developed, and there was an apparent action going on in the liquid.

At the expiration of 19 days the sample was examined for alcohol, and was found to contain only ·71 per cent., and at the end of a month it was again examined, and found to contain ·92 per cent. and one-tenth per cent. of acid.

It was obvious from this result that the soil was unsuited for the growth and propagation of the wine yeast cells. The sample was now diluted by the addition of water until the percentage of glucose was reduced to 18 per cent. This change of condition, however, had little influence in promoting the action of the cells, and the percentage of alcohol at no time afterwards was found to exceed 1·04 per cent.

At the end of several weeks a new form of fungoid growth was found to have been developed in the liquid, and a great mass of fresh cells produced, whose action appeared to have completely superseded the alcoholic ferment, and when the sample was next examined it was found to contain no alcohol whatever, but 2·80 per cent. of acid.

Two malt extracts were prepared, and the glucose present was made up in each case to about 30 per cent. To one sample wine ferment was added, and to the other malt ferment. The experiments were conducted, so far as was practicable, under the like conditions; but the results were somewhat different, the proportion of alcohol produced in the sample to which the

malt ferment had been added having exceeded the quantity produced in the other; and the spirit produced in the samples was perceptibly different in flavour.

Although this experiment is not regarded as conclusive, still it is worth recording, as the result tends to the same conclusion as that indicated by the results obtained in some of the other experiments, in showing that the different ferments have their favourite soils, and that they flourish best in those natural to them.

The results of the experiments would probably bear a more general conclusion in indicating a comparative inactivity of fungoid spores, unless when they meet with a soil that is favourable to their growth and development.

XXXIV.—*On Acetic and Formic Acid obtained from Human Urine during the Chemical Decomposition of Urochrome.*

By J. L. W. Thudichum, M.D.

1. *Preliminary Notes.*—Proust was the first to obtain acetic acid, or as he termed it "vinegar," by the decomposition of extract of urine. It was subsequently again obtained by Liebig from putrid urine, and believed by him to be a product of decomposition of the colouring matters. He did not obtain it from fresh urine, and believed that the other products of the decomposition of urochrome, the pitchy resins first described by Proust, could not be obtained from fresh urine, but were products of putrefaction. On p. 140 of the eleventh report of the Medical Officer of the Privy Council, 1869, I have enumerated the products of the chemical decomposition of urochrome, and amongst the volatile products I have enumerated acetic acid and uncertain volatile acids. Amongst the latter I have now recognized formic, and small quantities of higher acids. Formic acid had been repeatedly found to be an ingredient of human urine, but it had been declared an accidental product of the intentional ingestion into the stomach of certain substances which by decomposition in the economy yielded that acid. Moreover its presence had only been assumed on the basis of a few reactions

which did not exclude phenylic acid (which yielded similar reactions); it had not been found to be accompanied by acetic acid, which made the statement open to objection; and it had never been identified by its cardinal tests.

2. *Mode of obtaining Formic and Acetic Acid from Urine.*—These methods were first described by me in the Hastings prize essay, and may here be quoted:—

(*a.*) *From Fresh Urine.*—The urine is evaporated over the open fire to one-tenth, and filtered from the phosphates, urates, and gypsum. It is then slowly evaporated on the sand-bath, until a pellicle of urates forms. After cooling and filtering, it is evaporated on the water-bath to a syrup, and allowed to cool slowly over the water-bath, to effect a good crystallisation of chloride of sodium, urea, and other salts. The decanted syrup, mixed if necessary, with a little water, is treated with calcined magnesia, until alkaline, and until a filtered sample, treated with acetic acid and chloride of iron, does not give any immediate precipitate. The extract is then filtered. An extract thus prepared contains neither phosphoric nor uric acid, a diminished amount of sulphates, and a small amount only of chlorides. It contains free alkali and creatinine, but no magnesia. This extract of urine is put into a capacious beaker, and mixed with concentrated sulphuric acid, added, drop by drop, while the fluid is being agitated. A little uromelanine and some gypsum are precipitated in flocks. After filtration the fluid is diluted with water, and distilled in a capacious retort. When the fluid has been reduced to one-half, the black resin will be seen adhering to the sides of the glass, and to the platinum, which it is well to put into the retort to prevent bumping. The boiling is now interrupted, and the fluid allowed to cool. Fluid and resin are separated by decantation or filtration. The particles of resin are united by fusion in hot water. They are then washed and dried, and the resin is extracted from the black matter by solution in alcohol. The distillates containing the volatile acids, are treated as stated lower down.

(*b.*) *From Putrid Urine.*—Putrid urine is treated with a little lime in powder, or sawdust, and filtered. The dark brown filtrate is evaporated in an open dish over the open fire. Although it soon assumes a strongly acid reaction, nothing but ammonia passes away. All froth which rises during the evaporation is carefully skimmed off. When black particles begin

to appear on the surface it is allowed to cool, filtered, put into a retort, mixed with dilute sulphuric acid, and distilled. A mixture of hydrochloric, benzoic, acetic, and another acid passes over, together with a stinking matter, which deposits in flakes when the distillate is left to stand. The residue in the retort soon deposits the resin as a soft tar on the surface of the fluid, the sides of the vessel, and the platinum, put into the fluid for safe boiling. The resin is separated mechanically and by the filter, washed, and separated into its constituents by alcohol. The uropittine and uromelanine thus obtained present the same essential properties as those obtained from fresh urine.

3. *Treatment of the Distillates.*—Any solid benzoic acid (which occurs only in distillates from putrid urine, the distillates from fresh urine have all benzoic acid in solution) is filtered off. The fluid is then neutralized with powdered sodium carbonate and concentrated over the water-bath. When it becomes red and emits a powerful aromatic odour, it is allowed to cool and extracted with ether as long as this reagent extracts any of the essential volatile oil which yields the tyrosine reaction with mercuric nitrate on boiling. The solution of salts is then further concentrated to near crystallisation, and decomposed with an excess of sulphuric acid. The benzoic acid collects as a thick magma on the top of the fluid, and is filtered off. The liquid is mixed with water and distilled. The distillate is now already much purer, and is again neutralized, &c., and distilled once more. A pure solution of acids is now obtained which yields the reaction of both formic and acetic acid, but smells of butyric and caproic acid as well. Boiled with lead carbonate they yield lead salts, which sometimes crystallise, particularly with the help of a little ether, at other times remain as a colourless, transparent, thick and solid yet somewhat viscid mass. By no means, however varied, could pure crystals be obtained from the watery solution.

4. *Extraction of Neutral Lead Acetate by means of Alcohol.*—The watery solution of the first deposit from water was poured into alcohol. The mixture after standing some days deposited a large bulk of fine acicular crystals. They were isolated and allowed to drain on paper. When dry they contained (1·61 of moisture and) water of crystallisation, as follows:—

Analysis:—

(1.) 2·5725 grm. dried at 130°, fused, and frothed up, and

smelled faintly of vinegar. After many days' drying they lost 0·4052 grm. of water, leaving 2·1573 grm. of dry salt. Consequently the total loss was 15·81 per cent., and deducting from this the theoretical loss of $3H_2O$ = 14·2 per cent., there remains a slight excess of moisture as stated.

(2.) 2·1573 grm. of the dry salt were treated with sulphuric acid, and then cautiously heated to redness, acid being once more added during an interval of the ignition. There remained 2·005 Pb SO_4, while theory would require 2·0102. The dry salt therefore contains 63·66 per cent. of lead, *i.e.*, the theoretical quantity required by neutral acetate.

5. *Extraction of Half-basic Lead Acetate from the Mixture of Lead Salts.*—[$2(C_4H_6PbO_4)$ + PbO.] This salt has hitherto been obtained in chemical inquiries concerning acetic acid: (*a*) by heating the neutral salt to 280°, and keeping it at that temperature until the fused salt sets again; (*b*) by digesting the watery solution of two molecules of the neutral salt with one molecule of powdered lead oxide free from carbonic acid, until solution has taken place, and evaporating. The salt has an alkaline reaction. In the present research, however, this salt obtained as follows:—The acetic acid (containing formic) was treated with lead carbonate and boiled until saturated, and the filtrate was evaporated. At a certain point it crystallised entirely. After re-solution a small amount of salt crystallised first, and was separated and purified by recrystallisation. The saturated solution was now poured into a large amount of alcohol. Crystals deposited over night which were short prismatic needles of glassy lustre, gave on analysis the following results:—At 190° they lost a trifling amount of moisture, and remained constant; they were consequently anhydrous.

Analysis:—

(1.) ·8698 grm. on combustion left ·654 grm. of residue, being lead oxide = ·434 grm. equal to ·4028 Pb, and ·22 metallic lead, total Pb = ·6228 grm., or 71·60 per cent.

(2.) 1·1805 grm. left ·8766 grm. residue, being ·5456 PbO, equal to ·5064 Pb, and ·331 Pb, total Pb = ·8374 or 70·93 per cent.

Mean of these analyses = 71·26 per cent. Pb.

Required by the above formula 71·37 per cent.

Schindler obtained a hydrated crystallised salt of this compound, which contained two atoms of water. He poured the

saturated watery solution into an equal or double amount of alcohol (strength not stated), when the salt was deposited in pearly scales. At 90° they lost 2 per cent. of water, fused, and on cooling formed a colourless gum. This when heated further was transformed into a white mass, losing more water. These forms of pearly scales, colourless gum, and white mass were also obtained by heating the solution of the salt from urine on the water-bath and letting it stand.

The circumstance that the crystals in the foregoing experiment were anhydrous, admits of explanation by the fact that a large volume of strong alcohol was employed in their separation. They moreover admit of no theory if considered to have contained any formiate.

But the *third* and *fourth* crystallisations were evident mixtures of neutral acetate and formiate; the latter crystallised in little opaque granular groups, while the acetate crystallised with brilliant crystals. The third crystallisation contained little, the fourth much formiate. The *fifth* crystallisation had a remarkably homogeneous appearance, and was analysed.

(1.) 1·1230 grm. yielded 1·1050 grm. $PbSO_4$ = 67·22 per cent. of lead.

(2.) 1·215 grm. yielded 1·9280 grm. $PbSO_4$ = 67·67 per cent. of lead.

Mean = 67·44 per cent. of lead.

In a mixture yielding the half-basic salt the quarter-basic could also be formed, which requires 76·95 per cent. of lead. But the fact that the third and fourth crystallisations contained increasing quantities of formiate made it probable that the fifth also contained formiate, although in appearance it was quite homogeneous. This was indeed established by a special examination, which yielded the reduction tests: and in one experiment with sulphuric acid so much carbonic acid and carbonic oxide was obtained, that the conclusion was unavoidable that the mixture of crystals contained at least one half by weight of formiate. In the sixth crystallisation, which also appeared quite uniform, the following relations were found—

Analysis:—

4·1580 grm. yielded 4·1240 $PbSO_4$ equal to 67·74 per cent. Pb.

Consequently the lead had increased a little; the salt contained a little more formiate, which requires 69·6 per cent. of lead;

but even at the end no pure formiate could be obtained. The last mother-liquors contained small quantities of acid with less than the proportion of lead in the acetate. In short, in this instance the process of fractional crystallisation failed entirely to yield any pure product after the preponderance of acetate had ceased, and even the employment of alcohol did not effect that neat separation of formiate (insoluble) from acetate, (soluble in alcohol) which is advised in handbooks as if it were a fact; for the acetate was found to hold the formiate in solution even in alcohol, or to fall with it from the more concentrated solution.

6. *Barium Salts of the Volatile Acids from Urine.*—The lead salts having failed to afford the means of a neat separation of the acids, a new quantity of the acids was prepared and transformed into barium salts by boiling with barium carbonate. The solution was evaporated and when in a syrupy state was put aside for crystallisation. Crystalline crusts were slowly deposited, and removed. These first crystals were not analysed, but the next crystals (2nd crystals) were perfectly colourless and homogeneous and were analysed.

(1.) ·3258 grm. gave ·2992 grm. $BaSO_4$, equal to 53·99 per cent. of barium.

(2.) ·3998 grm. gave 0·3680 grm. $BaSO_4$, equal to 54·12 per cent. of barium.

Theory for acetate, 53·72 per cent. of barium.

Mean found, 54·05 per cent. of barium.

This crystallisation, therefore, consists of pure acetate. It yielded all cardinal reactions of acetic acid with precision, and was free from formic.

The mother-liquor was now allowed to stand and formed a crust on its surface. Underneath that crust large beautiful crystals of rhombohedral shape, the obtuse corners cut off by a hemitropic (round principal axis) rhombohedron of greater elongation, were formed. They were of glass-like lustre and transparency. Some were detached entire and analysed separately.

Analysis:—

(1.) ·7712 grm. lost at 110° ·1010 grm. aq., or 13·09 per cent. From this it might have been supposed that the crystals were a new hydrate of barium acetate, of the formula $C_4H_6BaO_4 + H_2O$,At. W. 291, requiring 12·37 per cent. of water but—

(2.) The ·6702 of dry salt yielded ·6362 grm. $BaSO_4$, equal to ·3736 Ba. or 55·74 per cent. The theory of the acetate requires 53·72 per cent. The dihydrated barium acetate should by direct combustion, without previous drying, yield 47·07 per cent. Ba. but—

(3.) ·7878 grm. (which frothed up on heating suddenly) left ·66 $BaSO_4$, equal to 49·25 per cent. Ba.

The crystals therefore contain, both in the anhydrous and dehydrated state, 2 per cent. Ba more than corresponds to acetate. The ordinary monohydrate of barium acetate, $C_4H_6BaO_4 + H_2O$, contains 6·59 per cent. aq., and 50·18 per cent. Ba. It was therefore probable that these crystals were not acetate, or not acetate only, and on examination it was found that they contained a considerable amount of formiate. The amount can be appreciated by putting the figures for Ba in acetate, crystals and formiate side by side—

Acetate requires	Crystals contain	Formiate requires
Ba 53·72 per cent.	Ba 55·74 per cent.	Ba 60·35 per cent.

The crystals correspond to a mixture of nine atoms of acetate with four of formiate, which requires 55·76 per cent. Ba. The form and stoichiometric relation of the water are probably an imitation of a new barium acetate dihydrate. *They show that barium acetate and barium formiate are isomorphous, and cannot be separated from each other by crystallisation in mixtures in which the atoms of formiate rise to more than one-third of the amount of atoms of the acetate.* The same was of course the case with the lead salts. Neither by distillation, nor by crystallisation of lead salts with and without alcohol, nor by crystallisation of barium salts, have I as yet obtained any pure formiate, although this salt is present in large quantity; but of the prevalent acetates pure crystallisations were obtained. I am therefore unable to determine directly the actual amount of formiates obtained as compared to acetates, but indirectly such determination may of course hereafter be made by destroying the formic acid, and distilling the remaining acetic. I estimate that upon five parts of acetic acid the urine yielded one part of formic.

7. *Determination of the Acetic and Formic Acid contained in the daily Urine of a Man.*—The total urine from eleven successive days of a healthy man was concentrated and distilled with sulphuric acid. A quantity of acid distillate was obtained, neutralized

with sodium carbonate and evaporated. The concentrated solution was again decomposed with sulphuric acid, and the benzoic acid separated. The liquid was again distilled, and the distillate boiled with lead carbonate. A quantity of salt was obtained which refused to crystallise, lost acetic acid during evaporation, and became at last partially insoluble in water. From a portion dibasic acetate crystallised. The whole was decomposed, and the amount of lead determined as sulphate. This weighed 8·007 grm., corresponding to 5·47 grm. of metallic lead. This corresponds to 8·59 grm. of lead acetate from urine of eleven days, equal to an excretion of 3·12 grm. in eleven days, or 0·288 grm. per day. I abstain from correcting the data for formic acid on account of what has been stated; its daily amount may be roughly estimated at ·05 grm.

8. *On the Conditions in which Acetic and Formic Acid may be contained in Urine.*—As these acids can only be obtained from urine by processes and agents which effect evident decompositions, such as those of urochrome, it is fair to allow that the volatile acids also may, like benzoic acid,* be products of the cleavage of more complicated substances. But it is impossible at present to say what the substances are, and whether the acids are not simply present in combination with some base or other. The latter view might indeed be held if the relative significance could be attributed to the following reaction of urine, which I observed several years ago, and inquired into at some length.

Fresh urine is treated with some milk of lime and filtered; it is then treated with ferric chloride as long as a precipitate is thereby produced, and a slight excess of ferric chloride is added. The filtrate from the ferric hydrate will be found to have a deep red colour, similar to that which ferric salts produce in formiates, acetates, benzoates, succinates, sulphocyanides, and other salts. The reaction has lately been ascribed to sulphocyanide, but for this I sought years ago without success. I find now that it is yielded also by kryptophanates. Now the urine contains ammonia, which would form with ferric chloride

* *Benzoic acid* is most probably a normal ingredient of human urine. This excretion further contains *a peculiar benzoyl-compound,* differing widely from hippuric acid, which, under the influence of cold concentrated hydrochloric acid, quickly splits up into benzoic acid and the body which I have described as *omi choline.*

some basic salt, and this also might produce the reaction; the distillate from fresh urine, indeed, shows the reaction beautifully with a drop of ferric chloride. It is, therefore, quite impossible at present to say whether this reaction is due to any organic acid, much less to which of those which are now all (succinic acid is also alleged by Meissner to be constantly present in urine) shown to be contained in urine.

When urine or its extract is mixed with a moderate quantity of sulphuric acid and boiled, a very peculiar state of things ensues, which is not generally understood. The ingredients are not in the presence of sulphuric acid, as it were, at all, but in that of a very slight chemolytic influence only, a kind of contact action. The sulphuric acid is at once enveloped by the attraction of urea,* and as long as urea is present no sulphate is formed, except that of ammonia, even on boiling. Although some benzoyl-compound is decomposed in the extract of urine, and benzoic acid is given out, yet much hippuric acid remains in solution unchanged, and crystallises after the extract has been boiled for hours. If the hippuric acid had been in presence of free sulphuric or hydrochloric acid it must have been decomposed entirely by half an hour's boiling. To the same preserving influence of urea is due the fact that in the distillates obtained during the decomposition of urochrome according to my method, which yields the acetic and formic acid, *no hydrochloric acid is ever found.* Such acid is only evolved by the addition of a great excess of sulphuric acid to extract of urine, and its effect and advent are unmistakably evident in the fluid. *The mixture becomes black*, and loses entirely its previously red colour. It deposits black charred matter, which differs *toto cælo* from uromelanine and the resinous urochrome products. From such charred urine no uromelanine and no pure products of any kind can be obtained. Now these particular conditions, more than anything else, incline me to the opinion that the acetic and formic acid are products of the decomposition of higher organic bodies, and not merely acids set free from salt by sulphuric acid. They escape simultaneously with the carbonic acid gas which is

* Presuming the urine to contain urea, which does not appear to be proved. If the urea, isolated by various processes, were the result of the splitting up of a more complicated body, then the neutralizing influence upon the sulphuric acid here alluded to would of course have to be exercised by this compound of high atomic weight.

evolved from the urea, and causes a continuous slight effervescence in the fluid. The sulphuric acid does not decompose the kryptophanic acid in the extract any more than the hippuric, *i.e.*, only a portion of it, and that certainly a small one. But when free hydrochloric acid appears the kryptophanic acid disappears, forming, in fact, the great bulk of the black matters in which such decomposing extract of urine abounds. These peculiar reactions must be carefully borne in mind by every one who would successfully study or comprehend these decompositions.

The foregoing research has been conducted by me for the Medical Department of the Privy Council, at the Pathological Laboratory of St. Thomas's Hospital.

XXXV.—*Researches on Leucimide, a Decomposition product of the Albuminous Substances and of Leucine.*

By J. W. L. Thudichum, M.D.

The products of the decomposition of albuminous substances by the usual process of Braconnot, before any leucine or tyrosine has been abstracted therefrom, are cautiously evaporated to dryness, and further dried by prolonged exposure to air. The residue is now stirred in a mortar with absolute ether, and then digested with the ether for several weeks in a bottle, and frequently shaken. The decanted solution, after distillation of the ether, leaves white crystals, which are further purified from an adhering syrup by washing with water and recrystallisation from boiling absolute alcohol.

Instead of the ether, alcohol may also be employed for the first extraction of the white crystals from the dried mixture. A dark alcoholic solution is obtained, which, after evaporation at a low temperature, on cooling deposits crystals in broom-like masses. These crystals are insoluble in water, and from this mother-liquor a considerable quantity of the matter composing these crystals is precipitated by the addition of water. After

washing on the filter, these flakes and crystals are easily soluble in boiling alcohol. The brown solution is decolorized by treatment with animal charcoal, and after concentration and standing, deposits colourless crystals in voluminous delicate masses. After drying they had the properties and composition of leucimide, hereafter described.

In several most laborious operations with large quantities of material (in one instance as much as fifty pounds of animal hair having been operated upon by seventy pounds of sulphuric acid, and the product after evaporation in a vacuum apparatus having been extracted by many gallons of ether and alcohol), only a few grammes of substance were obtained. These only just sufficed for establishing the identity of the substance with leucimide, whereupon the study of the properties of this body was continued upon material obtained by dehydration of leucine.

Leucine obtained from animal tissues by sulphuric acid and purified, was placed in a Florence flask and heated in an oil-bath, while a current of dry hydrochloric acid gas was passed through it. At the temperature of 210°—215° C., the crystals of leucine disappeared, and a brownish semi-fluid mass collected at the bottom of the flask. During the whole time the current of acid carried a quantity of water-vapour into the discharge tube and condensing flask attached, as also some oily drops. When the temperature of the oil reached 230° C., a copious white sublimate appeared in the neck of the flask. The action was then interrupted, and the product purified by extraction with water and repeated crystallisation from alcohol. By repeating the operation I have learned that it is advantageous to continue the heat to about 230° until the sublimate appears, as otherwise more leucine remains in the state of hydrochlorate; the resinous product can be treated with hot water directly, but it is easier to dissolve it first in a small quantity of alcohol and to pour this into a large quantity of water. The washed precipitate crystallises easily and pure from alcohol, while the water retains all other admixtures.

The products soluble in ether, can be obtained in the following manner and succession :—

Oil.—On gentle evaporation a yellowish brown oil is deposited in films and drops. It is easily soluble in ether, partially soluble in caustic potash. It is also found in the volatile

products, together with hydrochlorate of amylamine. The oil is insoluble in water, but very easily soluble with a yellow colour in free amylamine.

Amylamine.—From the concentrated water extract, and from the volatile oil this base is obtained by distillation with caustic potash. It is crystallised with hydrochloric acid, and purified by redistillation. The solution in water of the dry hydrochlorate is precipitated by bichloride of platinum, and some alcohol. The resulting light yellow compound left platinum.

Leucine-hydrochlorate.—The caustic mixture on cooling still deposits some leucimide, after removal of which a body crystallises in white hard granules. It is leucine-hydrochlorate of potassium, very little soluble in caustic-potash mixture, more easily soluble in, and not recrystallised from pure water.

Ammonia.—A vestige of this base is also sometimes obtained. If the oil be considered as the second leucic acid anhydride, the ammonia may be claimed as the product of decomposition of leucimide.

Physical and Chemical Properties of Leucimide.—The substance howsoever obtained crystallises in needles of the rhombic system, visible under high powers of the microscope. They are white, and of a dull, glistening, cotton-like appearance. When heated in a test-tube they fuse, and then sublime easily, the vapours condensing in voluminous clouds of most delicate needles.

They are insoluble in cold water, but a little soluble in boiling water, the solution becoming turbid on cooling. They are easily soluble in cold alcohol, more so in hot alcohol; a boiling saturated solution on cooling solidifies into a mass of crystals. The addition of large quantities of water to an alcoholic solution precipitates the leucimide almost completely in flakes. In ether leucimide is less soluble than in alcohol.

The crystals of leucimide are not changed by caustic ammonia or by concentrated caustic potash even on boiling. Cold concentrated hydrochloric acid also leaves them unchanged; on boiling a trace dissolves, which makes the solution turbid on cooling. Concentrated acetic acid keeps leucimide in solution, and yields it as a copious precipitate on the addition of alkali. Concentrated nitric acid also dissolves leucimide and leaves it unchanged even on evaporation.

Analysis led to the formula $C_6H_{11}NO$:—

			I.	II.	III.	IV.	V.
6C	72	63·71	63·64	62·78	63·62	63·93	„
11H.....	11	9·73	10·47	10·12	10·06	9·96	„
N.....	14	12·38					13·25
O.....	16	14·18					
	113	100·00					

I. Extracted by ether from preparation by first method.

II. Leucimide prepared by hydrochloric acid as above related from leucine extracted from human liver, gave the following results:—0·2338 grm. burned with copper oxide yielded 0·5384 grm. CO_2 and 0·2132 H_2O, equal to 62·78 per cent. of C. and 10·12 per cent. of H.

III. The matter was thereupon recrystallised from alcohol, when it assumed larger forms, and was free from smell and colour; 0·16 grm. burned with oxide of copper and metallic copper in the fore part of the tube, gave 0·3734 grm. CO_2, equal to 0·1018 grm., or 63·62 per cent. C, and 0·1457 grm. H_2O, equal to 0·0161 grm., or 10·06 per cent. H.

IV. 0·318 grm. gave 0·7456 grm. CO_2, equal to 0·2033 or 63·93 per cent. of C, with 0·286 grm. H_2O equal to 0·0317 grm., or 9·96 per cent. H.

V. After the preparation used in analyses III. and IV. had been crystallised, the mother-liquor was again condensed, and a last preparation obtained, which was used for the nitrogen determination. Of this 0·2556 grm., when burned with soda-lime gave 0·2387 grm. Pt., equal to 0·0337 grm., or 13·25 per cent. nitrogen.

Theoretical Considerations.—Leucimide, like leucine and leucic acid, may be supposed to contain a radical leucyl, $C_6H_{10}O$, homologous with lactyl. Its formation from leucine may be represented by the equation—

$$\underset{\text{Leucine.}}{\left.\begin{matrix}(C_6H_{10}^{H_2}O)''\\ H\end{matrix}\right\}N}_{O} = H_2O + \underset{\text{Leucimide.}}{\left.\begin{matrix}(C_6H_{10}^{H}O)''\\ H\end{matrix}\right\}N}.$$

The amylamine is due to the reaction—

$$C_6H_{13}NO_2 = C_5H_{13}N + CO_2.$$

While the leucine employed in the reaction should lose theoretically about 14 per cent. of weight by water, it actually loses

upwards of 20. About six per cent. are therefore lost in the collateral decompositions detailed above.

Leucimide was first observed by Bopp (Ann. Ch. Pharm. lxix, 28), afterwards by Hesse and Limpricht (*ibid.* cxvi, 201) and by Erlenmeyer and Schöffer (Verhandl. des Nat. Hist. med. Vereins zu Heidelberg, vol. 2, and Zeitschr. f. Chem. and Pharm. Erlangen, ii, 315), and by the latter three observers termed the nitrile of leucic acid. Kohler (Ann. Ch. Pharm., cxxxiv, 367) afterwards obtained it from synthetically prepared leucine, and the above observations are confirmatory of his results, and of the identity of synthetical leucine from valeraldehyde and hydrocyanic acid with that obtained from albuminous substances by sulphuric acid.

The circumstances under which leucimide is formed in the latter process are questionable. That it is not formed by the action of alcohol and lime upon the leucine mixture, as was probable from the manner in which it had been obtained by Bopp, but is a contemporary product of leucine and tyrosine, I have shown by extracting it repeatedly from the freshly-prepared leucine mixture. It may possibly be due to the prolonged influence of sulphuric acid upon already formed leucine in concentrated boiling mixtures.

One of the remarkable properties of leucimide is its indifference towards acids and alkalies. Although constructed upon the type ammonia, the properties therefrom derived are almost entirely lost. It resembles in this respect the secondary amides of the univalent acid radicals, such as acetyl. Diacetamide, $\left.\begin{matrix}C_2H_3O\\C_2H_3O\\H\end{matrix}\right\}N$, imitates the construction of leucimide, by containing two univalent acetyl groups in place of the two atoms of hydrogen which in leucimide are replaced by the bivalent leucyl, and, like leucimide, diacetamide has lost the power of combining with acids. Monacetamide, $\left.\begin{matrix}C_2H_3O\\H_2\end{matrix}\right\}N$, on the other hand, retains the properties of a weak ammoniacal base.

When leucimide is extracted from the leucine mixture, it is frequently mixed with a considerable amount of a substance rich in sulphur. It is difficult to decide whether the sulphur of this substance is a residue of the original sulphur contained in the albuminous substance, a product of the influence of sul-

phuric acid and of the prolonged influence of alkali upon the mixture containing sulphates during evaporation, or of the sulphuretted hydrogen by which the excess of lead employed for purification has been removed from the mixture. I have isolated this sulphur compound on several occasions. It differs from leucimide by its greater solubility in ether, and by forming larger leaves of crystals of the aspect of mother-of-pearl. It yields a black precipitate on boiling with a solution of lead in caustic alkali, and in one analysis it contained 19·9 per cent. of sulphur; it decomposes during drying above 80° C., and when a concentrated solution in alcohol is heated beyond saturation, it forms brown drops of resin, a product of decomposition. This substance, which I have termed thiotherine, can therefore not be mistaken for leucimide, and can be separated from it by boiling with caustic potash, which leaves leucimide unchanged and crystalline.

By treatment of an alcoholic or ethereal solution of leucimide with sulphuretted hydrogen gas, this compound is not obtained. The great mass of leucimide crystallises unchanged, and free from sulphur; but a small quantity of a sulphur-compound is always formed, which has the odour of garlic, and adheres to the unchanged leucimide with great pertinacity. The compound is extremely volatile. It is possibly a sulphuretted aldehyde, and requires further examination. When to an alcoholic saturated solution of leucimide tincture of iodine is added, and the mixture boiled, slight discoloration ensues. Hydriodic acid is developed in small quantity. The mixture, after addition of excess of caustic potash and much water, deposits white crystals.

XXXVI.—*On the Production of the Sulphates of the Alcohol-Radicals from the Nitrites by the action of Sulphurous Acid.*

By Ernest T. Chapman.

Mr. Miles H. Smith and myself, whilst working on the reactions of nitric and nitrous ether, observed that nitrite of amyl is very readily attacked by sulphurous acid, even when in aqueous solution, or when combined with ammonia, in the form of acid sulphite of ammonia.

When nitrite of amyl is added to strong aqueous solution of acid sulphite of ammonia, a very violent reaction takes place, gases are evolved, and neutral sulphate of ammonia is precipitated. The liquid product of the reaction is complex, nor do I know any method by which it may be resolved into its proximate constituents. The reaction with strong aqueous sulphurous acid is less violent. Free sulphuric acid is amongst the products, nitric oxide is evolved, and again a complex liquid product is formed.

When sulphurous acid gas is passed into nitrite of amyl it is rapidly absorbed. The nitrite changes in colour from yellow to green, from green to blue; it then begins to effervesce, and at the same time becomes very hot and boils violently. Nitric oxide is evolved in abundance, and a yellow liquid product remains; this liquid cannot be distilled without decomposition; it contains no nitrogen. When an attempt is made to distil it with water, the oily liquid found in the distillate consists principally of amylic alcohol. When the liquid is distilled *per se* it blackens, gives off sulphurous acid, and yields a complex distillate, which contains, amongst other things, valerianate of amyl.

From the above it will be obvious that any attempt to obtain an insight into the nature of the reaction, by an examination of the liquid product, was very unpromising; I therefore determined to attack the subject quantitatively. With this object I determined the nature and amount of the gas evolved by the action of excess of sulphurous acid on a known weight of the nitrite. The result proved that the gas evolved consisted of pure nitric oxide, and that the whole of the nitrogen present in

the nitrite escaped in this form. The details of this and all other determinations mentioned in this paper will be found in an appendix at the end. I also determined the amount of sulphurous acid required to decompose a given quantity of the nitrite. This determination was made by observing the quantity of sulphurous acid which disappeared when an excess of sulphurous acid acted on a known quantity of nitrite. The result proved with sufficient accuracy that one atom of sulphurous acid acted upon two atoms of nitrite of amyl, and liberated two atoms of nitric oxide. Lastly, the alteration of weight which nitrite of amyl undergoes by the reaction was determined. This result confirms the supposition that the reaction consists in the replacement of two atoms of nitric oxide by one of sulphurous acid. The result may, therefore, be formulated as follows :—

$$\left.\begin{matrix}C_5H_{11}ONO\\C_5H_{11}ONO\end{matrix}\right\} + SO_2 = \left.\begin{matrix}C_5H_{11}\\C_5H_{11}\end{matrix}\right\} SO_4 + 2NO.$$

The resulting liquid compound had, therefore, the composition of neutral sulphate of amyl.

To prepare it, nitrite of amyl is placed in a retort, the beak of which points upwards, and is adapted to an inverted condenser, so that any liquid which may be volatilized and condensed will return to the retort. To the tubular of the retort a cork and bent tube are adapted, so that the end of the tube dips beneath the surface of the nitrite; pure dry sulphurous acid gas is now passed into the liquid, and the retort gently warmed to start the reaction. If the warming be omitted the sulphurous acid is absorbed for some time, without any reaction occurring, but when the reaction does start it is with almost explosive violence, whereas if the liquid be warmed at first, the reaction starts at once, and proceeds regularly and evenly. When the effervescence which accompanies the reaction has quite ceased, the retort should be heated in a water-bath, the stream of sulphurous acid being still continued; lastly, the stream of sulphurous acid is to be discontinued, and a stream of carbonic acid or hydrogen substituted for it; this serves to expel the excess of sulphurous acid. It is desirable to fill the retort and condenser with carbonic acid before commencing to pass the sulphurous acid; the advantage of this is that the air, the oxygen of which would unite with the nitric oxide and

sulphurous acid, is expelled. The liquid product of the reaction is of a straw-yellow colour, and somewhat syrupy consistence. It may be heated up to about 110° C. without showing any signs of alteration, but if kept for any length of time at a temperature somewhat above this, it begins to blacken, and soon decomposes with an appearance of ebullition. As before stated, it cannot be distilled in any way; it is very readily decomposed by water; if boiled with water for a few hours it is completely resolved into amylic alcohol and sulphuric acid; long standing with water in the cold produces the same result. I do not think it can even be washed without decomposing to a greater or less extent. Boiled with caustic soda it yields amylic alcohol and sulphate of soda. Treated with strong hydriodic acid it yields sulphuretted hydrogen, water, free iodine, and iodide of amyl. Bichromate of potash and sulphuric acid cause it to yield valerianic acid. Its leading characteristic in short is, its extreme readiness to split up into sulphuric acid and amylic alcohol in presence of the elements of water. Its specific gravity is somewhat less than that of water.

Sulphurous acid and nitrite of butyl react upon each other in a manner precisely analogous to that of sulphurous acid and nitrite of amyl, but the resulting product is even more unstable, blackening at the heat of the water-bath. The product has not been examined in detail, but it appears to react in a manner strictly analogous to the corresponding amyl compound.

Nitrite of ethyl and sulphurous acid do not very readily react upon each other, at least at the common temperature. There are numerous practical difficulties, chiefly connected with the extreme volatility of the nitrite, in operating at a higher temperature, and I have not yet had the time or opportunity to overcome them.

The first point which suggests itself in considering the foregoing results is this—are these compounds properly speaking sulphates of alcohol-radicals, or are they only isomeric therewith? The reaction of the amyl compound with water is very different from that ascribed to neutral sulphate of ethyl under similar circumstances, but is strictly analogous to that of neutral sulphate of methyl.

It would obviously be of great interest to compare the sulphate of ethyl obtained from nitrite of ethyl and sulphurous acid with that obtained from ether and anhydrous sulphuric

acid; at any rate it is beyond all doubt that the sulphate of amyl, prepared from the nitrite, does not form any acid analogous to the isethionic acid when it is boiled with water; it splits up entirely into sulphuric acid and amylic alcohol, as a determination in the appendix will fully prove.

The question of the possibility of isomerism among sulphates of alcohol-radicals dependent on differences in linking the constituents together, is one which has now to be considered. I may leave on one side all cases of isomerism dependent on the existence of isomeric organic radicals. Representing our alcohol radical by R then, and assuming sulphur and oxygen to be both diatomic elements, and that there is no difference in the value of the two "bonds," or attaching powers, which they each respectively possess, it will be apparent that two very distinct compounds may exist; in one both the molecules of organic radical are linked to oxygen directly, and by oxygen to sulphur; in the other one of the radicals is attached directly to sulphur, and the other indirectly through the oxygen. They may be formulated as follows; the former would be:—

$$R—O—O—S—O—O—R,$$

and the second

$$R—S—O—O—O—O—R.$$

It may, I think, be safely predicted, that whatever be the formula of the sulphate of ethyl produced by the action of anhydrous sulphuric acid on ether, the formula of the sulphate of amyl prepared from the nitrite, resembles the first of the above formulæ, that is, the amyl is linked to the sulphur by oxygen, and not directly. In the case of the sulphate of ethyl, I should incline to the opposite belief: for it is difficult to see when ether, itself a perfectly saturated body, unites with a diatomic body, how it can do so without splitting into a peroxide of ethyl, and ethyl.

Now, if peroxide of ethyl and ethyl were to attach themselves to a diatomic body, the one would obviously be directly attached, and the other attached by its oxygen. Now the radical SO_3 is a diatomic radical, and we have no reason whatsoever for supposing that when it unites with other bodies the point of union is alone on the side of the oxygen. With at least equal probability we may assume that it unites both by

its sulphur and by its oxygen. Now let us further assume that the ethyl of the ether goes direct to the sulphur, and the oxide of ethyl to the oxygen, we should then have a body of the second formula—

$$Et—S—O—O—O—O—Et.$$

Now if a body of this kind were acted upon by water, it would naturally split up into isethionic acid and alcohol; it would in fact be no sulphate of ethyl at all, but isethionate of ethyl. It is not, however, necessary to assume that the whole of the ethyl produced by the splitting up of the ether shall go to the sulphur, and the whole of the oxide of ethyl simultaneously produced to the oxygen; they may, and probably do, unite somewhat irregularly. If I may use so materialistic an expression, they may unite just as they happen to come in contact, and in this case we should obtain a mixed body, which would present precisely the reactions ascribed to sulphate of ethyl. This view of the case derives considerable support from the fact already mentioned, that sulphate of methyl resembles the above-described sulphate of amyl in its reactions, and not the sulphate of ethyl, for sulphate of methyl is formed direct from methylic alcohol, that is, from oxide of methyl plus hydrogen; the methyl is therefore, most probably, united to the sulphur by oxygen.

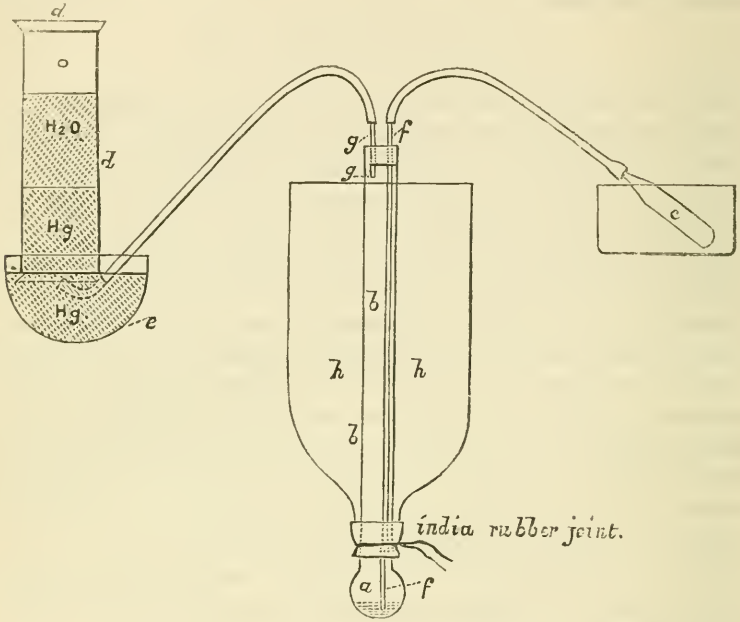
Appendix.

The nitrite of amyl used in the following investigation was carefully prepared from pure amylic alcohol. It boiled constantly, and I have every reason to believe was perfectly pure.

The determinations of the amount of sulphurous acid absorbed by a given quantity of the nitrite, of the amount of nitric oxide evolved, and of the weight of the resulting liquid, were all made in one and the same operation. Preliminary experiments had been made in which one or other of these points had been roughly ascertained.

I constructed an apparatus represented in the annexed woodcut. The tube, *b b*, was made of light thin glass. It was expanded into the bulb, *a*, and fitted into the vessel, *h h*, by an india-rubber joint, which, though water-tight, could be readily dismounted. The mouth of it was closed by a tightly-fitting cork, through which passed two narrow glass tubes, the one,

f f, reaching to the bottom of the bulb, the other, *g g*, only passing through the cork. Both tubes were perfectly straight. To use the apparatus, the tube, *b b*, was first detached from *h h*,



Apparatus employed to determine the amount of Nitric Oxide evolved from Nitrite of Amyl by the action of Sulphurous Acid, and the amount of sulphurous acid absorbed by the nitrite.

filled with carbonic acid, and, together with the tubes, *f f* and *g g*, was carefully weighed. Next a small quantity of nitrite of amyl was introduced by means of a very fine funnel through *f f*, and the tube *b b*, was weighed again. The difference gave the weight of nitrite of amyl employed. Next the tube was reconnected with *h h*, and *h h* filled with ice and salt. *f f* was now connected by means of an india-rubber tube with *c*, a stout sealed tube drawn off to a very fine point, and containing liquefied sulphurous acid. It had previously been carefully weighed. It also was surrounded by ice and salt. The tube, *g g*, was connected with the delivery-tube which dipped under the surface of a mercury-bath, over which was inverted the cylinder, *d*. *d* had been entirely filled with mercury and inverted into the trough, then water had been let up into it, and, finally, oxygen; so that it was abou half-full of the gas, and about

one-half of the remaining space was occupied by water, the other by mercury. Matters being disposed as here described, the point of the sealed tube, *c*, was broken off inside the india-rubber tube, and the ice and salt removed from around it. The liquefied sulphurous acid soon began to vapourize. As soon as this was the case, the bulb, *a*, containing the nitrite was warmed over a spirit lamp. The reaction soon started, and proceeded quite regularly and smoothly to its close; though it was obviously completed long before all the sulphurous acid was evolved. The tube, *b b*, surrounded by ice and salt, proved a most efficient condenser. Of course, the sulphurous acid was in great excess. It therefore swept all the nitric oxide evolved into *d*, where, meeting at once with oxygen and water, it was rapidly converted into nitric acid, the sulphurous acid at the same time being converted into sulphuric acid. More oxygen was from time to time passed into *d*. When the evolution of sulphurous acid from *c* had quite ceased, *c* was removed, together with the little piece of glass broken off in opening it, and both together weighed. The difference between this weight and their weight when full gave the quantity of sulphurous acid employed. Next a stream of carbonic acid was sent through the pipe, *f f*, so as to drive all the gases evolved out of the apparatus and into *d*. The tube, *b b*, was then detached from its connections and weighed. The difference between this weight and its former weight indicated the difference of weight caused in the nitrite by the reaction. Lastly, the mixed nitric acid and sulphuric acid in *d*, were determined by neutralization of one-fourth of the aqueous contents of *d* with carbonate of baryta. Of course nothing but nitrate of baryta remained in the solution. The excess of carbonate of baryta, together with the sulphate of baryta formed, was filtered off and well washed, the washing being added to the filtrate, which latter was evaporated to dryness and the dry residue weighed. In another fourth of the liquid the amount of sulphuric acid was determined by precipitation as sulphate of baryta. Calculating the quantity of sulphurous acid unused from the quantity of sulphate of baryta found, and deducting this from the known weight of the sulphurous acid taken, the difference will represent the sulphurous acid used. From the quantity of nitrate of baryta it is easy to calculate the quantity of nitric oxide evolved. The following are the details of this operation:—

Nitrite employed	5·44 grms.
SO_2 taken	3·894 „
Residue in A after operation	5·521 „
Nitrate of baryta yielded by one-fourth of the aqueous contents of *d*	1·495 „
Sulphate of baryta from ditto	2·216 „

From these numbers the following amounts of sulphurous acid consumed and nitric oxide liberated may be calculated. They are given in per cents. of the nitrite taken :—

NO found.	SO_2 used.	Residue, supposed sulphate of amyl.
25·27	26·82	101·49 per cent.

Now, if the reaction proceeded according to the equation on page 416, it would have required the following percentages :—

NO required.	SO_2 required.	Sulphate of amyl required.
25·64	27·35	101·71

It will be observed that the quantities both of nitric oxide found, and of sulphurous acid used, are slightly smaller than those required by theory. This would obviously be the case if a small quantity of the nitrite were volatilized with the escaping gases, and, despite every precaution, a very minute quantity of the nitrite would be sure to escape in this manner. Even not taking this fact into account, the accordance between the observed and calculated numbers is as close as that furnished by any of the common methods of analysis, and is at the same time very far indeed from corresponding with any other interpretation of the reaction.

A determination of the amount of sulphuric acid liberated by digesting the sulphate of amyl with water was made. The sulphate was sealed up with about fifty times its own volume of water in a capacious glass tube; the lower part of the tube was heated by a boiling saturated salt-bath for about six hours. It was then opened, its contents transferred to a flask, rinsed out, and the rinsings also put into the flask, and the whole boiled for a few minutes to expel the amylic alcohol. It was then precipitated with chloride of barium, and the sulphate of baryta so obtained weighed.

Sulphate of amyl taken	1·143 grm.
Sulphate of baryta found	1·1113 „

This indicates that the liquid has yielded 40·06 per cent. of SO_4. Sulphate of amyl should contain 40·34. It is therefore obvious that no part of the sulphate can have been converted into compounds analogous to isethionic acid.

NOTE appended Nov. 29th, in consequence of some doubts being expressed at the Chemical Society when the paper was read, as to the accuracy of the method of estimation adopted.

The method of estimating nitric oxide and sulphurous acid mentioned in the text, was experimentally investigated before being employed. The points investigated were, whether the presence of mercury interfered with the estimation; whether the presence of sulphurous acid interfered; and whether the process gave trustworthy and constant results. The result was to prove that if care were taken always to keep a large excess of oxygen and a large volume of water present throughout the whole of the process, neither the presence of sulphurous acid, nor that of mercury interfered in any way. If but little water is present the process is not trustworthy as far as concerns the nitric oxide, but the sulphurous acid determination may still be depended upon. It is necessary that the water employed should be a little above the ordinary atmospheric temperature, and that sufficient time be allowed to complete the reaction. It is desirable to let the apparatus stand in a warm room over night before completing the determination. This is not the place for a detailed account of trial experiments; I will therefore only say that I have operated on known quantities of nitric oxide under the circumstances indicated, and have arrived at the conclusion that the method described in the text may be implicitly relied on to yield results not more than $2\frac{1}{2}$ per cent. from the truth. The error is always in deficit, and seldom reaches 2 per cent. The nitric oxide was obtained in measured quantities by acting on known weights of nitrate of potash with excess of an acid solution of proto-sulphate of iron.

XXXVII.—*On the Composition of the Hyposulphites.*

By E. A. Letts, Daniell Scholar of King's College, London.

Though the salts of hyposulphurous acid have been comparatively well studied, much difference of opinion exists as to their chemical constitution. Rose (*Traité de Chimie Analytique*, p. 1475) states that an atom of water is retained by all the hyposulphites, which is essential to their composition, and can only be expelled when the salts themselves are decomposed. On the other hand, Pape (Jahresb. für 1864, p. 57), Kessler (Pogg. lxxxiv), and some other chemists, maintain that most, if not all the hyposulphites can be obtained in the anhydrous condition. Dr. Schorlemmer (Chem. News, May 28, 1869) thus quotes Pape's view:—"Pape (Pogg., Ann. cxxii, 408) found all the hydrogen present in the form of water of crystallisation, which, with care, could be expelled without the salt being decomposed, but the last portion of water is driven off at a temperature only a few degrees below that at which decomposition begins. By heating the sodium, barium, and potassium salts to 215° C., they can be obtained anhydrous, while at 5° higher they decompose; the lead salt is anhydrous at 100° C., but at a few degrees higher it blackens."

The discrepancies in the above statements may perhaps be accounted for in the following manner:—

First, the determination of sulphur in these salts is sometimes a matter of considerable uncertainty, and though many experiments were performed to ascertain where the difficulty lay, no really satisfactory conclusion was arrived at.

Moreover it has been found impossible to fix definitely the decomposing point of many hyposulphites; thence perhaps Pape's assertions may have arisen. Take for example the sodium salt; this salt, if *rapidly* heated, will bear a temperature of 233° C., without apparent decomposition, but if heat be applied more gradually, the salt actually decomposes at 100° C.

The following experiments were undertaken, with a view to ascertain whether hydrogen was to be regarded as an essential constituent of the hyposulphites.

The salts submitted to experiment were the sodium, barium, strontium, magnesium, lead, nickel, and cobalt hyposulphites.

A specimen of pure crystallised hyposulphite of sodium was first analysed.

The sodium in the crystallised salt was estimated as sulphate. Strong sulphuric acid was poured upon a weighed quantity of the salt in a porcelain crucible, the cover being inverted in the crucible. In this state when the action (which at first was very violent) had subsided, the crucible was cautiously heated. Sulphur and sulphurous anhydride, together with a considerable quantity of sulphuretted hydrogen, were evolved. When these had ceased to come off, the excess of sulphuric acid was expelled, and the remaining salt, after being repeatedly heated with carbonate of ammonia, weighed.

As a mean of three experiments, 18·46 per cent. were obtained, 18·5 per cent. being the theoretical quantity ($Na_2S_2O_3 5H_2O$).

The estimation of sulphur as already stated, was a matter of considerable difficulty.

The following methods were tried :—

(1.) Oxidation with red fuming nitric acid.

(2.) Oxidation with aqua regia.

(3.) Oxidation with chlorate of potass and nitric acid.

(4.) Oxidation with permanganate of potass (both volumetrically and gravimetrically).

(5.) Oxidation with bichromate of potass.

(6.) Rose's nitrate of silver method.*

(7.) Another plan suggested itself, based on the reaction of the hyposulphites with nascent hydrogen. Here they are decomposed, their sulphur uniting with the hydrogen, to form sulphuretted hydrogen.

In applying this method the hyposulphite dissolved in a little water, and some granulated zinc were placed in a flask fitted with a cork, through which passed two tubes, one for introducing hydrochloric acid, the other for conducting the sulphuretted

* To the hyposulphite dissolved in water (in cold solution) excess of nitrate of silver is added. This occasions the precipitation of hyposulphite of silver, which, as it is well known, is decomposed almost directly it is produced, into sulphide of silver. This, when weighed, represents half of the sulphur. The remaining half existing in the solution as sulphuric acid is precipitated in the ordinary manner with a barium salt, and weighed.

(1) $2AgNO_3 + Na_2S_2O_3 5Aq = Ag_2S_2O_3 + 2NaNO_3 + 5Aq.$ and

(2) $Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4$.

hydrogen produced by the reaction, mixed with excess of hydrogen, into a set of Mitscherlich's bulbs, containing a solution of potass, which absorbed the sulphuretted hydrogen. The escaping gas was afterwards passed into a solution of acetate of lead, so that no sulphuretted hydrogen escaped.

On the whole the best general results were obtained by employing the red fuming nitric acid. The practical details are as follows :—

The salt to be experimented upon is placed in a tube, and lowered into the acid contained in a plain retort. The action is usually violent, though not explosive. When this somewhat moderates, the sulphur separates in yellow flakes, and the retort placed vertically is very gradually heated in a water-bath, starting with cold water, and gradually raising the temperature to boiling; in this way all the sulphur is oxidized. The contents of the retort are next washed into a beaker, and the solution evaporated as far as possible over a water-bath, then diluted, boiled, and whilst boiling, the sulphuric acid produced by the oxidation is precipitated with chloride of barium. If the excess of nitric acid is not evaporated off, a couple of days may be required for the complete separation of the sulphate of barium.*

The water in the crystallised salt was determined by placing a quantity (4·913 grms.) in vacuo over sulphuric acid, and weighing at intervals. In about two months, 1·790 grm. had been lost, the remainder, when heated to 100° C., lost only ·005 grm. more. The total loss was therefore 1·795; this represents 36·5 per cent; according to the formula, $Na_2S_2O_3 5H_2O$, five molecules of water equal 36·3 per cent. It is therefore perfectly evident that the whole of the water contained in this salt is expelled, either in vacuo over sulphuric acid, or at 100° C. In order to verify this, another experiment was made in the same manner. In this latter 36·3 (being exactly the five molecules) was lost.

Hyposulphite of Sodium dried at 100° C., gave on analysis 28·8 per cent. sodium (estimated as sulphate), and 40·2 (the mean of five experiments) of sulphur. The formula of the anhydrous hyposulphite requires 40·5 per cent. sulphur, and 29·1 per cent. of sodium.

* Tetrathionate of barium is soluble in nitric acid, but gradually decomposes into sulphate.

The results may be thus compared :—

	Found.	Calculated $Na_2S_2O_3$.
Sodium	28·8	29·1
Sulphur	40·2	40·5
Water expelled at 100°C.	36·3	36·5($5H_2O$)

Hyposulphite of Barium was the next salt experimented upon. It was prepared by mixing hot and tolerably strong solutions of chloride of barium and hyposulphite of sodium, and allowing the mixture to cool. Under these circumstances brilliant white laminæ were precipitated of a beautiful silvery appearance, which were washed several times with distilled water, and dried upon blotting paper.

The barium was estimated as sulphate. Four determinations gave—

I.	II.	III.	IV.	
51·1	51·0	50·9	50·9	per cent. Ba.

In the formula BaS_2O_3,H_2O, the barium amounts to 51·3 per cent.

The sulphur was estimated in the same manner as that already detailed for the sodium salt. But as the sulphate of barium formed by the oxidation of this salt is insoluble, and the proportion of barium present is to the sulphur as 1 to 2, the $BaSO_4$, when weighed, represented half the sulphur. The other half was precipitated separately with chloride of barium.

The barium and sulphur thus estimated may be compared with the theoretical quantities, thus :—

	Found.	Calculated BaS_2O_3,H_2O.
Barium.....	51·0	51·3
Sulphur	23·9	23·9

From these estimations it is evident that the salt was pure hyposulphite of barium, containing one molecule of water. In order to determine whether this water could be expelled, 0·5 gramme of the salt was left in vacuo over sulphuric acid for three or four days, and then heated to 100° C. in a water oven ; the salt had then lost ·039 grm. This represents 6·7 per cent. of water. In another experiment, 3·397 grm. being taken, 0·228 was lost; this also represents 6·7 per cent.

The one molecule in BaS_2O_3,H_2O also equals 6·7 per cent. It is therefore evident that the salt loses all its water at 100° C.

The results obtained by the analysis of the hyposulphite of barium dried at 100° C. were—

	Found.	Calculated BaS_2O_3.
Barium.....	54·9	55·0
Sulphur	25·5	25·5
Water expelled at 100° C.	6·7	6·7(H_2O)

Hyposulphite of Lead.—To a tolerably concentrated solution of pure hyposulphite of soda, a solution of acetate of lead was added (at a temperature of 60° C.), till the precipitate first formed ceased to be redissolved. The mixture was then rapidly filtered, and cooled in a vessel containing cold water. Abundant starry masses of pure white crystals* were gradually formed and precipitated. They were washed in cold water and dried on blotting paper. The lead in this salt was determined as sulphate; 64·2 per cent. and 64·6 per cent. were thus obtained. The formula PbS_2O_3 requires 64·8. The sulphur was estimated in the same manner as in the barium salt, the sulphate of lead, the result of the oxidation of the salt, representing half the sulphur. The other half was estimated separately in the filtrate from the sulphate of lead.

The following are the results:—

	Found.	Calculated PbS_2O_3.
Lead.....	64·4	64·8
Sulphur	19·9	20·0

It is therefore evident that hyposulphite of lead crystallises as an anhydrous salt.

Hyposulphite of Strontium was prepared by mixing equivalent quantities of solutions of hyposulphite of sodium and chloride of strontium; on cooling, large hexagonal crystals were formed. The strontium in these was estimated as sulphate, 30·4 per cent. of strontium being thus obtained. The formula $SnS_2O_3,5Aq$ requires 30·3.

The sulphur was determined as in the lead and barium salts, the sulphate of strontium formed representing one half of the

* If these conditions be not strictly observed, it is possible the hyposulphite will not be quite white. It was after many experiments on its preparation that a good method was obtained.

sulphur. Two experiments were made; they both gave 22·0 per cent.; 22·1 is the quantity required by theory. For the water, 0·5 gramme of the salt was heated in a water-oven. It lost 1·239, representing 24·7 per cent., the formula of the crystallised salt being $SrS_2O_3 5H_2O$. Four out of the five molecules H_2O equal 24·9. It thus appears that only four out of the five molecules are expelled at 100° C.; but as it was thought possible that the remaining molecule H_2O might be expelled at a somewhat higher temperature, an experiment was made to ascertain this fact. For this purpose a quantity of the dried salt was placed in a Liebig's drying tube, and heated in a bath of fused paraffin, whilst a current of dry air was drawn over it by an aspirator, the water being collected in a weighed chloride of calcium tube.

10·235 grms. of the salt, dried at 100° C., was placed in the drying tube, and the paraffin-bath very gradually heated. At each rise of about 10° the Liebig's tube and chloride of calcium tube were disconnected and weighed. When the temperature reached 200° C., 0·421 grm. had been lost. This loss equals 4·1 per cent. Now 8·2 represents the molecule of water remaining in the salt; this loss then is one-half of the water present. The salt dried at 200° C., must therefore be represented as $2SrS_2O_3,H_2O$, and this will not part with its water without decomposition.

A curious phenomenon was observed whilst making this experiment. As the temperature rose the salt lost its white colour, and became quite yellow, the depth of the colour augmenting with the temperature; but upon cooling, it regained its white appearance.

Hyposulphite of Magnesium was obtained in tufts of transparent colourless prismatic plates, on evaporating its solution produced by the decomposition of strontic hyposulphite and magnesic sulphate in equivalent proportions, from which the sulphate of strontium had been separated by filtration. The magnesium (estimated as sulphate) gave—

I.	II.	III.
9·94	9·86	10·0 per cent.

The formula $MgS_2O_3,6H_2O$, requires 9·83 per cent. magnesium.

The sulphur was determined in the usual manner (as in the sodium salt). This gave—

I.	II.	III.
26·2	26·0	25·9 per cent. S.

The formula $MgS_2O_3,6H_2O$ requires 26·2. The salt lost at 100°C.—

I.	II.	III.
22·96	22·96	22·8 per cent.,

corresponding to a little more than half the water contained in the crystallised salt. This result was fully confirmed by the estimation of the magnesium in the salt dried at 100° C.

An experiment was made in the same manner as detailed for the strontium salt, to ascertain whether further water could be expelled at temperatures above 100°, but the salt was decomposed.

Hyposulphite of Nickel was prepared by mixing solutions of strontic hyposulphite and sulphate of nickel, filtering off the sulphate of strontium thus produced, and concentrating the solution in vacuo over sulphuric acid. When of very small bulk, large crystals of a beautiful dark green colour were produced.

They seemed very stable in air, not altering in appearance when kept five or six months. The nickel (as sulphate) was found to amount to—

I.		II.
21·4	and	20·7

The formula $NiS_2O_36H_2O$, requires 21·1 per cent.

The sulphur was determined by oxidation with nitric acid, and weighing as sulphate of barium.

I.		II.
22·6 per cent.	and	23·0 per cent. S.

were thus obtained. The formula $NiS_2O_3,6H_2O$ requires 22·9. To determine the water, a quantity of the salt was placed in vacuo over sulphuric acid. It however slowly decomposed. The decomposition occurred rapidly when the salt was heated to 100° C.

Hyposulphite of Cobalt was obtained in the same manner as the nickel salt, using sulphate of cobalt in the place of the sulphate of nickel. The solution was pink when dilute, but when much concentrated, formed a dark blue syrup, from which the hyposulphite of cobalt separated in a dark red crystalline mass, which was deliquescent in air. The cobalt was estimated

as sulphate; this amounted to 21·2 per cent. The formula $CoS_2O_3,6H_2O$ requires 21·5 per cent. The results of the sulphur estimation were not satisfactory.

This salt was even more unstable than the nickel hyposulphite, and decomposed when simply kept in a stoppered bottle, it was therefore found impossible to determine the water.

By the experiments above described, I am led to the conclusion that hydrogen is *not* a necessary constituent of the hyposulphites. Commencing with the sodium salt we find that it crystallises with six molecules of water, and that the whole of these are given off at 100° C., or in vacuo over sulphuric acid. Pape (Pogg. Ann. cxxii, 408) asserts that a temperature of 215°C. is necessary to expel the last molecule of water from this salt. The barium salt crystallising with only one molecule of water, can be obtained anhydrous in the same manner. The lead salt crystallises free from water, its formula (as it crystallises) being PbS_2O_3. The strontium salt is somewhat more complex in the arrangement of its molecule. From its analysis it would seem to crystallise with five equivalents of water. Of these four may be expelled at 100° C., and at a higher temperature (200° C.) half a molecule more is given off, but the remaining half must be constitutional, as immediately above this temperature the salt decomposes. It is therefore probable that the molecule of this salt should be formulated thus, $2(SrS_2O_3),10H_2O$, nine molecules only of water being expelled without decomposition of the salt. Kessler (Pogg. Ann., lxxxiv. 274) asserts that strontium hyposulphite crystallises with six equivalents of water (instead of the five found by these experiments), and that it retains one at 180° C. The magnesium salt loses at 100° C. only three out of the six molecules of water which it contains; the other three do not appear to be expelled till decomposition of the salt has commenced. The cobalt and nickel salts decompose so readily, that they are not well suited for experiments in this direction.

XXXVIII.—*On the Heat Developed in the Combination of Acids and Bases.* (Second Memoir.)

By Thomas Andrews, M.D., F.R.S., Hon. F.R.S.E., Vice-President of Queen's College, Belfast.

[From the Transactions of the Royal Society of Edinburgh, Session 1869–70.]

In a paper communicated to the Royal Irish Academy in 1841, I gave an account of a large number of experiments on the heat disengaged when acids and bases, taken in the state of dilute solution, enter into combination, and when bases, insoluble in water, are dissolved in dilute acids. The following general conclusions or laws were deduced from those experiments :—

Law 1.—The heat developed in the union of acids and bases is determined by the base and not by the acid, the same base producing, when combined with an equivalent of different acids, nearly the same quantity of heat; but different bases, different quantities.

Law 2.—When a neutral is converted into an acid salt, by combining with one or more atoms of acid, no change of temperature occurs.

Law 3.—When a neutral is converted into a basic salt, by combining with an additional proportion of base, the combination is accompanied with evolution of heat.*

Three years later I laid before the Royal Society of London the results of an experimental investigation of the heat developed when one base is substituted for another in chemical compounds. The law deduced from this inquiry is implicitly involved in the foregoing, of which it may indeed be regarded as a necessary consequence. It was enunciated in the following terms :—

Law 4.—When one base displaces another from any of its neutral combinations, the heat evolved or abstracted is always the same, whatever the acid element may be, provided the bases are the same.†

Finally, the law of metallic substitutions, first announced in

* Transactions of the Royal Irish Academy, vol. xix, p. 228.

† Philosophical Transactions for 1844, p. 21.

the "Philosophical Magazine" for August, 1844, was thus stated in a paper published in the "Philosophical Transactions" for 1848.

Law 5.—When an equivalent of one and the same metal replaces another in a solution of any of its salts of the same order, the heat developed is always the same; but a change in either of the metals produces a different development of heat.

In 1845 a paper appeared by Graham on the heat disengaged in combinations, the second part of which refers to the heat produced when hydrate of potash is neutralised by different acids.* The results arrived at by this distinguished chemist exhibit a close agreement with those contained in my first communication to the Royal Irish Academy.

The concluding part of the elaborate memoir of MM. Favre and Silbermann on the heat disengaged in chemical actions is chiefly devoted to the same subject. A large number of experiments are described, which are nearly a repetition of those I had previously published. Their results bear a general resemblance to those given by myself in 1841, but they widely differ in the details. The authors of this able memoir fully recognize the accuracy of my fourth law, which asserts the equality of thermal effect when one base is substituted for another. "M. Andrews," they observe, "avait en effet établi que, quelque soit l'acide d'un sel, la quantité de chaleur dégagée par la substitution d'une base à une autre pour former un nouveau sel est la même, lorsque l'on considère les deux mêmes bases."†

In a preceding paragraph of the same memoir, the authors object to what they conceive to be my first law, and state that it is not in accordance with the results of their investigations. As the question is one of some importance, I may perhaps be permitted to quote the passage in the original language. "Ses conclusions, savoir: que la chaleur dégagée par l'équivalent d'une même base combinée aux divers acides est la même, ne s'accordent pas avec les résultats de nos recherches, et ne nous paraissent pas pouvoir être admises." No doubt, through inadvertence, MM. Favre and Silbermann have here given an inaccurate statement of my first law. It did not declare that

* Memoirs of the Chemical Society, vol. ii, p. 51.

† Annales de Chimie et de Physique 3eme serie xxxvii, p. 497 (1853).

precisely the same amount of heat is disengaged by all the acids in combining with the same base, but that the heat is determined by the base, "the same base producing, when combined with an equivalent of different acids, *nearly* the same quantity of heat." A comparison of the results of MM. Favre and Silbermann with those in my original memoir will show that I had fully recognized and described the deviations from the other acids, exhibited, on the one hand, in excess, by sulphuric acid, and on the other, in deficiency, by tartaric, citric, and succinic acids. "If we refer," I remarked, in the original memoir of 1841, "to the first, second, and fourth tables, as being the most extensive, from the large number of soluble compounds formed by potash, soda, and ammonia, it will be observed that sulphuric acid developes from 0°·8 to nearly 1° more than the mean heat given by the other acids; while tartaric, citric, and succinic acids fall from 0°·4 to 0°·55 short of the same. A minute investigation of the influence of the disturbing sources of heat will no doubt discover the causes of these discrepancies. The high numbers for sulphuric acid are probably connected with that acid's well known property of developing much heat when combining with successive atoms of water. All the other acids develope nearly the same amount of heat in combining with the same base, the greatest divergences from the mean quantity being, in the case of potash, + 0°·24, and − 0°·13; in that of soda, + 0°·26, and − 0°·14; and in that of ammonia, + 0°·17 and − 0°·05. These differences are almost within the limits of the errors of experiment."*

But although there is a superficial agreement between my original results and those of MM. Favre and Silbermann, they will be found, when examined closely, to differ widely in detail, and on points of great importance. I had found that oxalic acid disengages almost exactly the same amount of heat in combining with the soluble bases as hydrochloric, nitric, and many other mineral acids, and this observation I have always regarded as one of the main foundations of Law 1. MM. Favre and Silbermann, on the contrary, have inferred from their experiments that "the following organic acids—oxalic, formic, valeric, and citric—disengage sensibly the same quantity of heat, but it is less (plus faible) than that given by the foregoing mineral acids"—among which they enumerate the nitric and

* Transactions of the Royal Irish Academy, vol. xix, p. 240.

hydrochloric. According to my experiments, no distinction of this kind can be admitted between acids derived from the mineral and organic kingdom, inasmuch as oxalic acid developes at least as much heat in combining with the bases as hydrochloric, nitric, and several other strong mineral acids.

The experiments to be described in this paper were made some years ago, but their publication has been deferred from accidental circumstances. I have, however, recently repeated a few of the more important of them, with a slightly modified form of apparatus. The solutions were taken in so dilute a state that the heat disengaged never exceeded 3°·5 C. A standard solution of sulphuric acid was prepared and carefully analysed, by precipitating a given weight with a soluble salt of barium, and weighing the sulphate of barium. The strength of the alkaline solutions was adjusted with great care by means of this standard acid. The same solution of each alkali was employed in all the experiments, and the quantity used in each experiment was determined by careful weighing. The acid solution was of such a strength that, after being mixed with the alkali, an excess of two or three per cent. of acid was present. The alkaline solution was contained in a light glass vessel, in which a large platinum crucible holding the acid was carefully floated. By giving a rapid rotation, by means of a light stirrer, to the acid solution in the platinum crucible, a perfect equilibrium of temperature was soon established between the two liquids. The initial temperature of the solutions was usually about 1°·5 below that of the air, and the final temperature of the mixture about 1°·5 above it. The corrections for the heating and cooling action of the surrounding medium were determined with great care. The mechanical process of adding the acid to the alkaline solution produced no change of temperature, and as the heat disengaged in the combination raised the liquid almost instantly to the maximum temperature, the whole correction required was for cooling. The first temperature was read one minute after the addition of the acid to the alkaline solution, the mixture being stirred during the whole of that time. If δ represents the correction, and ϵ the excess of temperature above the air in centigrade degrees, the value of δ will be given by the following expression:—

$$\delta = \epsilon \times 0°{\cdot}012.$$

As a proof of the accuracy of the method of mixture adopted

in this inquiry, I may mention that, being desirous to know whether the dilute acids employed in these experiments produced any change of temperature when mixed with water, I made the experiment with nitric acid by the method just described, substituting water for the alkaline solution, with the unexpected result of a fall of 0°·01. On varying the conditions of the observation, so as to obtain a larger effect, it was ascertained not only that a diminution of temperature had actually occurred, but that the observed fall represented approximately its true amount. When hydrochloric acid of equivalent strength was diluted to the same extent, an elevation of temperature of 0°·05 was produced.

The accuracy of experiments of this kind, where the whole thermal effect observed amounts only to 2° or 3°, depends greatly on the thermometer employed. Unless its indications are perfectly trustworthy in every part of the scale, the labour of the inquirer will only end in disappointment. I have therefore taken every precaution to secure this important object. The tube of the thermometer was calibrated and divided with care, according to an arbitrary scale, by means of a dividing instrument contrived for the purpose, and provided with a short screw of great accuracy made by Troughton and Simms. The divisions, etched finely on the glass, corresponded to about 0°·05 C., and the readings could be made with certainty to less than 0°·01. The division of the scale, corresponding to 0°, was determined from time to time in the usual way; and another point, about 30° C., was fixed by comparison with four other thermometers similarly constructed, whose scales extended from the freezing to the boiling-point of water. The readings of these four instruments, when reduced to degrees, rarely differed from each other within the limits to which they could be read, or 0°·02. The reservoir of the thermometer used in these experiments was 75 millimetres long, and, when immersed in the liquid, occupied nearly its entire depth.

As some uncertainty always exists with regard to the thermal equivalent of glass vessels, I made two sets of comparative experiments—one with a thickly-varnished copper vessel, and the other with a vessel of platinum. The mean result of these experiments coincided almost exactly with the result obtained when the glass vessel was employed.

The weight of the glass vessel which contained the alkaline

solution was 58 grammes, and corresponded thermally to 11·4 grammes of the solutions formed. The thermal equivalent of the reservoir of the thermometer and of the stirrer was 0·9 grammes. The alkaline solution weighed 160 grammes, and contained the equivalent of 1·738 gramme of SO_3. The acid solution weighed 42·5 grammes. Hence the entire thermal value of the apparatus, in terms of the solution formed was—

Solution	202·5
Glass vessel	11·4
Thermometer and stirrer ..	0·9
	214·8 grammes.

A correction (additive) of $\frac{1}{240}$ was made to the direct readings for the mercury in the stem of the thermometer. The results are given to thousandths of a degree, but this apparent minuteness is due to the reduction of the indications of the arbitrary scale to degrees.

The following table gives the mean results of the new experiments, the acids being arranged in the order of their thermal action—

Acid.	Potash.	Soda.	Ammonia.
Sulphuric acid	3°·378	3°·353	2°·976
Oxalic acid.....	3°·058	3°·040	2°·648
Hydrochloric acid....	3°·021	2°·982	2°·623
Nitric acid	2°·993	2°·929	2°·566
Acetic acid.....	2°·852	2°·832	2°·492
Tartaric acid	2°·732	2°·710	2°·376

It is interesting to observe how closely the results in the three vertical columns agree relatively with one another. The acids follow in the same order under each base, and even the differences in the amount of heat disengaged by the several acids in combining with the different bases approximate in many cases closely to one another. Thus the heat given out when sulphuric acid combines with potash exceeds that given out when oxalic acid combines with the same base by 0°·320, the corresponding differences in the case of soda and ammonia being 0°·313 and 0°·328. If, in like manner, we compare the differences between the heat disengaged by the acetic and tartaric acids, we fall upon the numbers 0°·120, 0°·122, and 0°·116.

Even in the case of oxalic, hydrochloric, and nitric acids, which disengage so nearly the same amount of heat, the same order is observed with the three bases. It must be particularly remarked that the oxalic acid disengages from 0°·022 to 0°·058 more heat in combining with these bases than the hydrochloric acid, and from 0°·065 to 0°·111 more than the nitric acid. The conclusion of MM. Favre and Silbermann, that the organic acids (oxalic, formic, acetic, &c.) disengage sensibly less heat than the mineral acids, is thus entirely disproved; and the original results recorded in my work of 1841, according to which oxalic acid disengages at least as much heat as nitric, phosphoric, arsenic, hydrochloric, hydriodic, boracic, and other mineral acids (with the exception of the sulphuric acid) are fully confirmed. Tartaric, citric, and succinic acids, it is true (as was also shown in the same work), give out about $\frac{1}{14}$th less heat than the average of the other acids, but acetic and formic acids fall scarcely $\frac{1}{30}$th below the mean, and oxalic acid is always above it. These results, in all their main features, are fully corroborated by the experiments recorded in this paper, which were performed with a more perfect apparatus and a more exact thermometer than I had at my command in my earlier investigations. A reference to the same paper will show that, while acids, differing so widely from one another as oxalic, phosphoric, arsenic, nitric, hydrochloric, and boracic acids, scarcely present any sensible difference in the quantities of heat which they disengage in combining with the bases; and while of the other acids examined, sulphuric acid (and probably also sulphurous acid) presents an extreme deviation of about $\frac{1}{8}$th above the mean, and the tartaric acid group a deviation of about $\frac{1}{30}$th below it; the bases, on the contrary (and the subsequent researches of Favre and Silbermann have confirmed this result), differ altogether in thermal power from one another. Thus equivalents of the oxides of magnesium and of silver give out 4°·1 and 1°·8 of heat respectively in combining with nitric acid, the former oxide having therefore 2·3 times the thermal power of the latter. Yet, as is well known, both these bases fully saturate the acid, and the resulting solutions are even neutral to test-paper. For these reasons, I have no doubt whatever that the first law, as enunciated in 1841, is the expression of a true physical law, and that in the combination of acids and bases in presence of water the heat disengaged

is determined by the base and not by the acid. It is true that in this, as in similar physical inquiries, experimental results cannot immediately be obtained free from complication or disturbing influences. The same remark applies to the experimental proof of the great law discovered by Dulong and Petit, which connects the specific heats and atomic weights of the elementary bodies, and also to that of the remarkable relations discovered by Kopp between the composition and boiling points of many organic liquids. We have already seen an illustration of one of these disturbing influences, in the fact that dilute nitric acid, when mixed with water, gives a slight fall of temperature, hydrochloric acid, a rise; and the differences of specific heat in the solutions formed will, to a small extent, modify the results. But the cause of the higher thermal power of sulphuric acid I have not been able to discover, and future researches must decide whether it depends upon some disturbing cause, or (which is less probable) upon its possessing an exceptionally high thermal power. One condition is, however, essential, or Law 1 will not apply. The acid and base must be capable of combining when brought into contact, and of forming a stable compound. In the paper so often referred to, I showed that hydrocyanic acid and potash, which fail to fulfil this condition, do not disengage the normal amount of heat when mixed; and the same observation will doubtless be found to apply to a large number of metallic oxides, which form unstable compounds with, and imperfectly neutralize, the bases.

As regards the experimental proofs of the other laws, even those of the fourth law, the truth of which is admitted by MM. Favre and Silbermann, they are only approximative, and here also we meet occasionally with peculiar and unexpected results. Thus a slight fall of temperature occurs, as Hess showed long ago, in the conversion of the neutral sulphate of potash into the acid salt; and I found, as indeed might have been expected from their alkaline reaction, that in the conversion of the ordinary phosphates and arseniates into supersalts, a disengagement of heat occurs, amounting to about one-seventh of that disengaged in the formation of the salts themselves. In other cases results, at first view startling and apparently anomalous, will be found to be strictly in accordance with the general principles already laid down. In the formation of double salts there is no disengagement of heat—a prin-

ciple announced in 1841, and which ought perhaps to be enunciated as a distinct law, although it is implicitly involved in Law 2. Again, if tribasic phosphoric acid or arsenic acid is added in fractional portions to a solution of potash till the subsalts are formed, the heat disengaged on each addition of acid corresponds to the amount of acid added; but after this point has been reached, the disengagement of heat follows a different law. Pyrophosphoric acid, on the other hand, behaves in the same way as nitric and most other acids, when added in successive portions to solutions of potash or soda; equal increments of heat being evolved for equal additions of acid, till the pyrophosphate of potash or soda is formed.*

Appendix.

In the following tables I have given the results described in this communication and those of 1841 in a form which admits of comparison with one another, and with those of MM. Favre and Silbermann. I have also added a few determinations recently made by M. Thomsen of Copenhagen.† It will be seen that the original experiments of 1841 exhibit, on the whole, a fair agreement with those now communicated to the Society. From the small scale on which they were performed (the whole weight of the solutions after mixture being less than 30 grammes), the imperfect form of the apparatus, and the uncertainty of the thermometric indications, I have indeed been surprised to find them so near the truth. The results of MM. Favre and Silbermann do not exhibit the precision which might have been expected from the high character of those experimentalists, and from the accuracy of other parts of their great work. The mercurial calorimeter employed by them appears to have been little adapted to its purpose; but after making due allowance for its imperfections, I am at a loss to account for the serious errors into which they have fallen. M. Thomsen's experiments have evidently been made with care, and his results agree comparatively with my own; but the absolute amount of heat obtained by him falls far short of what I have found. It is indeed much easier to obtain results rela-

* Transactions of the Royal Irish Academy, vol. xix, pp. 245–248. The observations of Graham confirm the statement that no heat is evolved in the formation of any double salt. Memoirs of the Chemical Society, vol. i, p. 83.

† Poggendorff's Annalen, cxxxviii, p. 78.

tively than absolutely correct. The numbers given in this paper will, I believe, be found rarely to differ *relatively* more than $\frac{1}{200}$th from the truth, but they may hereafter require a small correction in respect to their *absolute* value. That correction can, however, be scarcely more than $\frac{1}{50}$th of the whole amount, and I have little doubt that the number, for example, given by Thomsen to express the heat disengaged in the combination of soda with nitric acid will prove to be as far below the true number as that given by MM. Favre and Silbermann is above it.

TABLE I.—*Potash.*

Acid.	Andrews, 1841.	Favre and Silbermann.	Andrews, 1870.
Sulphuric	16330	16083	16701
Nitric	15076	15510	14800
Hydrochloric	14634	15656	14940
Oxalic	14771	14156	15124
Acetic	14257	13973	13805
Tartaric	13612	13425	13508

TABLE II.—*Soda.*

Acid.	Andrews, 1841.	Favre and Silbermann.	Andrews, 1870.	Thomsen.
Sulphuric	16483	15810	16580	15689
Nitric	14288	15283	14480	13617
Hydrochloric	14926	15128	14744	13740
Oxalic	14796	13752	15032	..
Acetic	14046	13600	14000	..
Tartaric	13135	13651	13400	..

TABLE III.—*Ammonia.*

Acid.	Andrews, 1841.	Favre and Silbermann.	Andrews, 1870.
Sulphuric	14135	14690	14710
Nitric	12440	13676	12683
Hydrochloric	12440	13536	12964
Oxalic	12684	..	13088
Acetic	12195	12649	12316
Tartaric	11400	..	11744

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The Meetings of the Society, for the reading and discussion of scientific papers, are held on the first and third Thursdays of every month, from November to June inclusive, excepting that in January there is only one Meeting, on the third Thursday of the month. The Chair is taken at eight o'clock precisely.

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STENHOUSE, JOHN, Ph. D., F.R.S.

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Burlington House, Piccadilly, W.

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Original Members admitted at the formation of the Society are marked *
Life Members are marked ‖.

Date of Election.	
Mar. 21, 1848	Abel, F. A., F.R.S., Royal Arsenal, Woolwich, S.E.
Dec. 18, 1854	Abel, J. S., Esq., Copiapo, Chili
April 7, 1856	Acland, Thomas J. Dyke, Esq., Sprydoncote, near Exeter
	Adie, Richard, Esq., B. 4, Exchange-buildings West, Liverpool
Feb. 18, 1864	Allen, Alfred Henry, Broomhall-park, Sheffield
Jan. 21, 1869	Allen, John Fenwick, Esq., Windleshaw, St. Helens, Lancashire
Mar. 26, 1854	Allen, F., Esq., Chemical Works, Bow common, and 13, Stainsby-road, East India-road, Poplar, E
	Anderson, Thomas, M.D., F.R.S.E., University, Glasgow
Feb. 23, 1841	‖*Andrews, Thomas, M.D., F.R.S., Queen's College, Belfast
Jan. 17, 1861	Apjohn, James, M.D., F.R.S, South-hill, Blackrock, Dublin
May 16, 1861	Arnold, Edward, Esq., Prince of Wales Road, Norwich
June 7, 1864	Arnot, William, Esq., St. Anne's-villa, Lasswade, N.B.
Feb. 17, 1870	Atcherley, Rowland T., Theydon Bois, Essex
Mar. 5, 1863	Atherton, J. H., Esq., Nottingham
Mar. 17, 1859	‖Atkinson, E., Ph. D., Royal Military College, Sandhurst, Farnborough-road
Jan. 16, 1862	Attfield, John, Ph. D., 17, Bloomsbury-square, W.C.
Feb. 17, 1870	Axe, F. W., Royal Veterinary College, Camden-town, N.W.
Dec. 15, 1851	Bachhoffner, G. H., Ph. D., 204, Marylebone-road, N.W.
Nov. 20, 1848	Bain, Alexander, Esq., University, Aberdeen
Dec. 1, 1856	Baker, William, Esq., County Analyst's Office, 46, High-street, Sheffield
Nov. 17, 1845	Balmain, William H., Esq., St. Helens, Lancashire
April 18, 1861	Bamber, H. K., Esq., 5, Westminster Chambers, Victoria-street, S.W.
Mar. 5, 1855	Bancroft, J. J., Ruthin, North Wales
Mar. 21, 1867	Barff, F. S., Esq., 16, North Audley-street, W.
April 21, 1859	Barford, James Gale, Esq., Wellington College, Wokingham, Berks
Nov. 17, 1851	Barnes, James B., Esq., 1, Trevor-terrace, Knightsbridge, S.W.
Dec. 7, 1865	Barnes, W. J., Esq., Starling-lodge, Buckhurst-hill, Essex
Feb. 4, 1869	Barrett, Edward L., Esq., 20, Spencer-road, St. John's Hill, New Wandsworth
Nov. 4, 1869	Barrett, W. F., Esq., The Woodlands, Isleworth, Middlesex
Feb. 18, 1864	‖Bassett, Henry, Esq., 12, South Crescent, Bedford-square, W.C.
Feb. 17, 1870	Bateman, Arthur H., 41, Seething-lane, Great Tower-street, E.C.
Feb. 7, 1861	‖Beadnell, Charles Edward, Esq., West Green-road, Tottenham, N.
Dec. 5, 1867	Beale, William Phipson, Esq., 6, Stone-buildings, Lincoln's-inn, W.C.
Mar. 3, 1864	‖Beanes, Edward, Esq., Cordwalles, Maidenhead, Berks
Dec. 1, 1864	‖Beauchamp, Lieut. C. S., care of Messrs. Grindlay and Co., 55, Parliament-street, W.
Nov. 17, 1851	Beesley, Thomas, Esq., Banbury
Jan. 20, 1870	Bell, James, Laboratory, Somerset House, W.C.
Jan. 19, 1865	‖Bell, J. C., Esq., Gilda Brook, Eccles, near Manchester
Dec. 3, 1863	Bell, J. L., Esq., Iron Offices, Newcastle-upon-Tyne
Mar. 1, 1866	Bell, Prof. Robert, Queen's College, Kingston, Canada West
Mar. 17, 1864	Bell, T. L. G., Esq., Vitriol Works, near Abbey Mills, Stratford, E.
Mar. 3, 1845	Bernays, A. J., Ph. D., Prof. of Chemistry, St. Thomas's Hospital, S.
Dec. 7, 1865	‖Bickerdike, W. E., Esq., Eagle Chemical Works, Oswaldtwistle, near Accrington
Jan. 20, 1870	Bird, Alfred, 366, Bristol-road, Edgbaston, Birmingham
Dec. 18, 1854	Bloxam, C. L., Esq., King's College, W.C.

Date of Election.	
June 16, 1859	Bloxam, Thomas, Esq., The College, Cheltenham
Feb. 2, 1865	Blunt, T. P., Esq., 4, Victoria-street, Shrewsbury
Dec. 18, 1848	Blyth, John, M.D., Queen's College, Cork
Feb. 23, 1841	*Blythe, William, Esq., Holland Bank, Accrington, Lancashire
Mar. 18, 1869	Bolas, Thomas, Esq., 2, Little Sutton, Turnham Green, W.
Feb 2, 1865	Bosanquet, R. H. M., Esq., Christchurch, Oxford
June 17, 1858	Bond, F. T., M.D., Hartley Institution, Southampton
May 15, 1869	Bottomley, J. T., Esq., King's College, W.C.
May 7, 1868	Bournes, Thomas, Esq., Hardshaw-street, St. Helens, Lancashire
April 20, 1865	Bowdler, A. C., Esq., Eagle Chemical Works, Oswaldtwistle, near Accrington
Nov. 6, 1862	Bowman, F. H., Esq., Halifax, Yorkshire
Dec. 16, 1869	Bowrey, J. J., Esq., 10, Stepney Causeway, E.
April 15, 1869	‖Braby, Frederic, Esq., Mount Henley, Sydenham Hill
April 7, 1859	Brady, H. B., Esq., 40, Mosley-street, Newcastle-on-Tyne
Dec. 1, 1864	Bray, John, Esq., High-street, Sheerness
May 6, 1850	Brazier, James S., Esq., University, Aberdeen
Dec. 15, 1845	Brodie, Sir Benjamin Collins, Bart., F.R.S., Cowley-house, Oxford
May 2, 1867	Brough, J. C., Esq., 6, St. George's-terrace, Gloucester-road, Kensington, W.
Dec. 20, 1866	Broughton, John, Esq., B. Sc., Government Cinchona Plantations, Madras
Dec. 7, 1865	Brown, A. Gardiner, Esq., 63, Trinity-square, Southwark, S.E.
Dec. 5, 1867	Brown, Dr. A. Crum, 4, Rillbank-terrace, Edinburgh
Feb. 3, 1859	Brown, Edwin, O., Esq., Royal Arsenal, Woolwich, S.E.
Mar. 21, 1861	Brown, E. Burton, M.D., Medical College, Lahore
April 2, 1863	Brown, J. M., Esq., East Herward Works, West Calder, by Edinburgh
April 19, 1866	‖Brown, J. T., Esq., Oxford-villa, Sudbury, Middlesex
Mar. 7, 1867	Brown, James Campbell, Esq., Royal Infirmary School of Medicine, Liverpool
Mar. 1, 1852	‖Buckton, G. B., F.R.S., Weycombe, Haslemere, Surrey
Dec. 20, 1842	Bullock, Lloyd, Esq., Hanover-street, Hanover-square, W.
Mar. 19, 1849	Burnard, C. F., Esq., Phœnix Chemical Works, Plymouth
Feb. 16, 1857	Burr, Thomas William, F.R.A.S., 15, Tibberton-square, Islington, N.
Mar. 19, 1868	Byramjee, Dr. Rustomjee, care of Messrs. Grindlay, 55, Parliament-street, S.W.
Mar. 18, 1841	Calvert, Frederick C., F.R.S., Gibbon-street, Bradford, near Manchester
Jan. 4, 1847	Campbell, Dugald, Esq., 7, Quality-court, Chancery-lane, W.C.
Feb. 5, 1863	Carew, R. R., Esq., Carpender's-hall, Watford, Herts
Jan. 17, 1853	Carteighe, John, Esq., 3, Hereford-square, Old Brompton
June 16, 1864	Carteighe, Michael, Esq., 172, New Bond-street, W.
Nov. 1, 1860	Cartmell, Rowlandson, Esq., Burton-on-Trent
Dec. 5, 1867	Carulla, F. J. R., Esq., 91, Pas de Julio, Buenos Ayres
Mar. 18, 1869	Catcheside, William Frederick, Esq., Laboratory, Fore-street, Hesham
June 4, 1868	Chance, Henry, Esq., Sherborne House, Warwick
Dec 21, 1865	Chapman, Ernest T., Esq., 21, Devonport-road, Shepherd's Bush, W.
Jan. 16, 1868	Chapman, Edward, Esq., Merton College, Oxford
Feb. 6, 1868	Charlesworth, Thomas, Esq., The Hollow, Leicester
Jan. 16, 1868	‖Child, G. W., Esq., Elmhurst, Great Missenden, Bucks
April 6, 1865	Chrispin, William, Esq., 39, King-street, Huddersfield
Mar. 3, 1856	Church, Arthur Herbert, Esq., Royal Agricultural College, Cirencester
Mar. 19, 1868	Clapham, R. Calvert, Esq., Walker Alkali Company's Works, Newcastle-on-Tyne
April 16, 1868	Clarke, Lieut. F. C. H. R. A., The Citadel, Plymouth
Feb. 16, 1852	Claudet, Frederic, Esq., 6, Coleman-street, E.C.
May 19, 1856	Clift, Samuel, Esq., Chemical Works, Bradford, Manchester
Mar. 18, 1869	Clowes, Frank, Esq., 15, Cornwall-place, Holloway, N.
Nov. 2, 1869	Cochrane, Matthew, Esq., 103, Peel-terrace, Glasgow

Date of Election.	
Feb 21, 1853	Coleman, Alfred, Esq., 32, Old Burlington-street, W.
Mar. 7, 1861	Coleman, J. J., Esq., North Wales Coal Oil Company, Leeswood Hill, near Mold
Dec. 5, 1867	Coleman, Alfred, Esq., 13, St. Mary-at-Hill, E.C.
Mar. 19 ,1863	Colman, Robert, Esq., Clapham-common, S.
May 5, 1864	Conisbee, T. S., Esq., 39 and 40, Herbert's-buildings, Waterloo-road, S.
Jan. 18, 1866	‖Conroy, Sir John, Aborfield Grange, Reading
Dec. 6, 1866	Cook, Dr. E. A., Heriot-hill-house, Edinburgh
May 18, 1857	Coomber, Thomas, Esq., 15, Southwell-street, Bristol
Mar. 1, 1866	Corfield, W. H., B.A., F.G.S., Medical Fellow of Pembroke College, Oxford, University College, Gower-street, W.C.
April 17, 1862	Courtauld, Julian, Esq., Bocking-bridge, near Braintree
Feb. 2, 1860	Crocker, Edwin, Esq., Seymour-villa, Hungerford-road, Holloway, N.
Dec. 21, 1841	Croft, Henry, Esq., King's College, Toronto, Upper Canada
Dec. 3, 1857	Crookes, William, Esq., F.R.S., 20, Mornington-road, Regent's-park, N.W.
Mar. 19, 1863	Crossley, William, Esq , Ormesby Iron Works, Middlesbrough-on-Tee
Dec. 17, 1857	Dale, John, Esq., Cornbrook, Hulme, Manchester
Jan. 16, 1862	Dale, J. G., Esq., Mersey Bank Chemical Works, Warrington
April 15, 1850	‖Danson, Joseph, Esq., 6, Shaw-street, Liverpool
Nov. 15, 1852	Darby, Stephen, Esq., 140, Leadenhall-street, E.C.
Feb. 21, 1867	Davey, R. R. F., Esq., War Office, Pall Mall S.W.
Feb. 1, 1866	‖Davies, Arthur E., Esq., 87, Sankey-street, Warrington
May 6, 1858	Davies, Edward, Esq., Laboratory, Royal Institution, Liverpool
June 7, 1866	Davis, E. H., Esq., 2, Harley-road, Brompton
Dec. 17, 1857	‖Davis, J. Frederick, Esq., F.G.S., 2, Harley-road, Brompton
Feb. 7, 1861	Davis, John, Esq., 4, Church-street, Spitalfields
May 20, 1844	Davy, Charles, Esq., New Park-street, Southwark, S.E.
	Deacon, Henry, Esq., Appleton-house, Widnes, near Warrington
Mar. 4, 1869	Day, James John, Esq., 53 Bedford-square, W.C.
Feb. 6, 1854	De Bussy, C., Esq., Paris
Mar. 3, 1859	Debus, Heinrich, Ph.D., F.R.S., Clifton College, Clifton, Bristol
April 1, 1869	Deering, W. H., Esq., Chemical Department, Royal Arsenal, Woolwich, S.E.
Feb. 7, 1843	‖De la Rue, Paul, Esq., Ekateringoff, near St. Petersburgh
Feb. 23, 1841	‖*De la Rue, Warren, Ph. D., F.R S., Observatory, Cranford, Middlesex, W.
Mar. 16, 1857	Dent, W. Y., Esq., Royal Arsenal, Woolwich, S.E.
June 2, 1859	De Rheims, Henry, Esq., 2, Bedford-terrace, Plumstead-common, Woolwich, S.E.
Dec. 6, 1866	‖Dircks, Henry, Esq., Whitehall Club, S.W.
Feb. 2, 1860	Divers, Edward, M.D., 81, Lansdowne-road, Kensington-park, W.
Dec. 18, 1862	Dixon, W. A., Esq., 25, Gordon-street, Glasgow
Mar. 5, 1868	‖Dowson, Dr. Edward, 117, Park-street, Grosvenor-square, W.
Mar. 17, 1859	Draper, Harry, N., Esq., 72, Leinster-road, Rathmines, Dublin
Feb. 23, 1852	Dresser, Christopher Leele, Esq., Leeds
May 1, 1854	‖Duffy, Patrick, Esq., Surveying General Examiner Office, Inland Revenue, Somerset House, W.C.
Dec. 17, 1863	Duncan, James, Esq., 5, Highbury-hill, N.
Feb. 16, 1860	Dupré, Frederick, Ph. D., 53, Burton-crescent, W.C.
Jan. 19, 1860	Dupré, Auguste, Ph. D., 53, Burton-crescent, W.C.
Dec. 17, 1863	Duppa, B. F., Esq., F.R.S., United University Club, Pall Mall East
Feb. 7, 1848	‖Edwards, John B., Ph. D., Royal Institution, Liverpool
Dec. 1, 1864	Ekin, Charles, Esq., Bath
Feb. 1, 1866	Epps, Franklin, Esq., 112, Great Russell-street, W.C.
May 1, 1862	‖Esson, William, Esq., Merton College, Oxford
Feb. 2, 1865	‖Estcourt, Charles, Esq., Newbury, Berks
Nov. 5, 1849	Evans, Henry Sugden, Esq., 60, Bartholomew-close, E.C.
Feb. 21, 1867	Eve, H. W., Esq , Wellington College, Wokingham, Berks

Date of Election.	
May 18, 1865	Fairley, Thomas, Esq., Grammar School, Leeds
Feb. 15, 1866	Ferguson, G. B., Esq., 14, South-square, Gray's-inn, W.C., and Altidore Villa, Cheltenham
Feb. 4, 1864	‖Ferreira, A. A., M.P.S., Rio de Janeiro, Brazil
April 21, 1859	Fewtrell, William Toplady, Esq., 41, Gower-place, Euston-square, W.C.
Dec. 5, 1867	Fiddes, W. W., Esq., 2, Southernhay, Clifton, Bristol
June 18, 1857	Field, Henry W., Esq., M.A.P.S.Phil., Royal Mint, E.
Dec. 21, 1846	Field, Frederick, Esq., F.R.S., 9, Belmont-park, Lee, S.E.
Feb. 4, 1869	‖Field, James John, Esq., Highgate, N.
Dec. 7, 1865	FitzHugh, Richard, Esq., Nottingham
Dec. 19, 1867	Fletcher, A. E., Esq., 21, Overton-street, Liverpool
June 7, 1866	Flower, W. F., Esq., Guy's Hospital, S.E.
June 16, 1859	Fogg, Thomas, Esq., 11, Lanark-villas, Clifton-road, Maida-hill, W.
Feb. 21, 1853	Foord, G., Esq., Australia
Feb. 21, 1853	‖Forbes, David, Esq., F.R.S., 11, York-place, Portman-square, W.
Dec. 6, 1866	Forrest, James, Esq., Lambard-cottages, Ashburnham-road, Greenwich, S.E.
April 6, 1865	Foster, Dr. M., jun., University College, W.C.
Mar. 3, 1856	Foster, G. C., Esq., University College, W.C.
Feb. 17, 1870	Francis, E., 22, St. Peter's-square, Hammersmith, and Charing Cross Hospital
Nov. 7, 1842	Francis, William, Ph. D., F.L.S., Red Lion-court, Fleet-street, E.C.
Dec. 29, 1847	‖Frankland, E., Ph. D., F.R.S., 42, St. John's-park-road, Haverstock-hill, N.W.
Mar. 21, 1867	Fraser, Dr. Angus, 193, Union-street, Aberdeen
Mar. 7, 1867	Freeman, J. Hersee, Esq., Stratford-house, Stratford, E.
April 19, 1865	Gale, James, Esq., 1, Buckland-crescent, Belsize-park, Hampstead, N.W.
April 5, 1852	‖Gale, Samuel, Esq., 338, Oxford-street, W.
Dec. 20, 1847	Galloway, Robert, Esq., Royal College of Science, Stephen's-green, Dublin
Mar. 17, 1851	‖Gamble, David, Esq., Gerard's-bridge, St. Helens, Lancashire
June 21, 1866	Gamgee, Dr. Arthur, Alva-street, Edinburgh
Feb. 23, 1841	*Gassiot, John Peter, F.R.S., Clapham-common, S.
Jan. 18, 1847	Gatty, F. A., Esq., Holland Bank, Accrington, Lancashire
Feb. 18, 1864	Gibbons, Sydney, Esq., Collins-street East, Melbourne
Dec. 9, 1869	Gibbs, Thomas, Esq., Bede Metal Company, Jarrow-on-Tyne
May 18, 1841	Gilbert, Joseph Henry, Ph. D., F.R.S., Harpenden, near St. Albans
April 3, 1862	Gill, C. Haughton, Esq., 9, Westbourne-road North, Barnsbury, N.
Dec. 18, 1848	Gladstone, John Hall, Ph. D., F.R.S., 17, Pembridge-square, Hyde park, W.
Nov. 3, 1851	Gladstone, George, Esq., Clapham common, S.W.
May 21, 1849	Glass, William, Esq., 37, Princes-street, Stamford-street, S.
Dec. 4, 1862	Gossage, William, Esq., West Bank, Widnes Dock, near Warrington
Dec. 3, 1868	Gowland, George R., Esq., 48, High-street, Sheffield
May 1, 1862	‖Graham, Charles, Esq., Berwick upon-Tweed
Feb. 19, 1863	Green, Joseph, Esq., Messrs. Rowntree and Co., Cocoa Manufacturers York
Jan. 16, 1868	Griess, Peter, Esq., F.R.S., Messrs. Allsops & Sons, Burton-on-Trent
Feb. 23, 1841	*Griffin, John Joseph, Esq., 22, Garrick-street, Covent-garden, W.C.
June 16, 1859	Griffith, George, Esq., 1, Woodside, Harrow-on-the-Hill
May 3, 1861	Griffith, Thomas, Dr., 14, Tudor street, Surrey-street, Sheffield
Dec. 17, 1857	Groves, T. B., Esq , Weymouth
April 2, 1868	Guthrie, Frederick, Ph. D., F.R.S.E., Royal School of Mines, Jermyn-street, S.W.
Feb. 3, 1859	Hake, T. Gordon, M.D., Alton-lodge, Roehampton, S.W.
Dec. 4, 1862	Hall, T. F., Esq., 29, Warwick-square, S.W.
May 3, 1866	‖Hall, Marshall, Esq., 3, Cleveland-terrace, Hyde-park, W.

Date of Election.	
Dec. 5, 1867	Hall, Thomas, Esq., B.A.
Feb. 3, 1859	‖Hambley, C. H. Burbidge, Esq.
Nov. 15, 1852	Hamilton, George, F.R.A.S., Queen's College, Liverpool
Feb. 7, 1857	Hanbury, Cornelius, jun., Esq., Plough-court, Lombard-street, E.C.
Jan. 21, 1858	‖Hanbury, Daniel, F.R.S., F.L.S., Plough-court, Lombard-street, E.C.
Dec. 16, 1844	Harcourt, Vernon, M.A., F.R.S., F.G.S., Nuneham Park, Abingdon
Feb. 3, 1859	‖Harcourt, A. Vernon, Esq., F.R.S., Christchurch, Oxford
April 16, 1863	‖Harcourt, L. Vernon, Esq., 47, Cadogan-place, S.W.
Mar. 2, 1857	‖Harley, George, M.D., F.R.S., 25, Harley-street, Cavendish-square, W.
June 20, 1861	Harris, W. H., Esq., Laboratory, Long Buckly Wharf, near Rugby
Nov. 2, 18 9	Harrison, George, Esq., 26, Havelock-square, Sheffield
Jan. 21, 1869	Hart, F. W., Esq., 8, Kingsland-green, London
Dec. 20, 1866	Hartley, Walter Noel, Esq., Royal Institution, Albemarle-street, W.
May 5, 1856	Harvey, Alexander, Esq., Govanhaugh Dye Works, Glasgow
Nov. 20, 1848	Hay, W. J., Esq., H.M. Dockyard, Portsea
Dec. 1, 1864	Haywood, Henry, Esq., Furness Iron and Steel Company, Dalton-in-Furness, Lancashire
Feb. 21, 1867	Hearder, Jonathan, Esq., Plymouth
April 20, 1865	Heathfield, W. E., Esq., 8, Wilson-street, Finsbury, E.C.
Dec. 18, 1854	Heaton, Charles W., Esq., Charing-cross Hospital
Feb. 23, 1841	*Heisch, Charles, Esq., Middlesex Hospital, W.
April 4, 1861	Henn, Rev. John, B.A., Lond., F.R.G.S., Commercial School, Manchester
Mar. 7, 1853	‖Henry, W. C., M.D., F.R.S., Haffield, near Ledbury
Feb. 21, 1853	Hepburn, J. G., LL.B., 16, Long-lane, Bermondsey, S.E., and Reform Club, S.W.
April 3, 1848	Heywood, J. S. C., Esq., Caledonian-place, Caledonian-road, N.
Mar. 15, 1852	Higgin, James, Esq., 22, Little Peter-street, Manchester
Jan. 20, 1870	Higgins, Clement, King's College, W.C.
Dec. 16, 1858	Hill, Alfred, M.D., Laboratory, Queen's College, Birmingham
Feb. 7, 1853	Hills, Frank C., Esq., Chemical Works, Deptford, S.E.
Mar. 18, 1858	‖Hills, Thomas Hyde, Esq., 338, Oxford-street, W.
April 15, 1858	Hindle, James, Esq., Sabden, Whalley, Lancashire
Jan. 20, 1870	Hislop, G. R., Engineer's Office, Gasworks, Paisley
April 6, 1865	‖Hobson, A. S., Esq., 3, Upper Heathfield-terrace, Turnham-green, W.
Mar. 4, 1858	Hobson, J. T., Ph. D., Laurel House, Tyldesley, near Manchester
	Hodges, John F., M.D., Queen's College, Belfast
Mar. 3, 1849	‖Hofmann, Aug. Wm., Ph. D., LL.D., F.R.S., Prof., 10, Dorothien Strasse, Berlin
Feb. 18, 1869	Holditch, E. D., Esq., 10, Bankside, Southwark, S.E.
May 4, 1865	Holzmann, Dr M., Marlborough-house, S.W.
Dec. 18, 1862	Hooker, John, Esq., Dean's-place West, Husley, Woking Station, Surrey
Dec. 9, 1869	Hopwood, G. Manly, Esq., 22, Grosvenor-square, All Saints, Manchester
Dec. 15, 1856	Horsley, John, Esq., Cheltenham
Feb. 18, 1869	Howard, Alfred K., Esq., Messrs. Muspratt Bros. and Huntley, Flint, North Wales
Dec. 20, 1842	Howard, Robert, Esq., Stratford, Essex, E.
Feb. 6, 1868	Hozier, Lieut., J. W., Junior United Service Club, Charles-street, St. James's, S.W.
Feb. 7, 1867	Hudson, J. W., LL.D., Somerleyton, Brixton, S.
April 19, 1866	Huggon, William, Esq., Park-row, Leeds
Feb. 23, 1841	*Hughes, F. R., Esq., Bo'ness, Linlithgowshire
Dec. 17, 1868	Hughes, John, Esq., 16, Penn-road-villas, Camden-road, Holloway, N.
Mar. 18, 1869	Hunt, Charles, Esq., London Gas Light Company, Nine Elms, S.W.
Dec. 15, 1851	Hunt, Edward, Esq., 6, Mouton-terrace, Moss-side, Manchester
Dec. 7, 1865	Hunter, John, Esq., Fountainville, Belfast
Mar. 21, 1861	Huskisson, H. O., Esq., 322, Gray's-inn-road, W.C.
Dec. 6, 1866	Huskisson, William, jun., Esq., 76, Swinton-st., Gray's-inn-road, W.C.
June 4, 1868	Hustler, William, Esq., Rosemerryn, Falmouth
June 18, 1863	Hutchinson, Rev. T. N., Hillmorton road, Rugby

Date of Election.		
Feb.	7, 1867	‖Ince, Joseph, Esq., 26, St. George's-place, Hyde-park-corner, S.W.
Dec.	16, 1869	Jefferson. S., Woodville-terrace, Woodhouse-lane, Leeds
Dec.	18, 1843	Jennings, Thomas, Esq., 10 and 11, Brown-street, Cork
May	6, 1858	Johnson Richard, Esq., 27, Dale-street, Manchester
April	7, 1856	Jolley, George, Esq., 13, Curzon-street, Mayfair. W.
May	11, 1841	‖Jones, Henry Bence, M.D., F.R.S., 31, Brook-street, Grosvenor-square, W.
Feb.	2, 1857	Jones, John, Esq., 16, Adelaide-terrace, Portishead, Somerset
Dec.	15, 1856	Jones, Hodgson, Esq., 67, Victoria-street. Westminster, S.W.
Mar.	16, 1865	Jones, George, Esq., 106, Leadenhall-street, E.C.
Jan.	1, 1844	Joule, James P., F.R.S., Cliff Point, Higher Broughton, near Manchester
April	6, 1865	Judd, William, Esq., 10, Bath-street, Leamington
Mar.	4, 1858	‖Kane, Sir Robert, F.R.S., 51, Stephen's-green, Dublin
June	2, 1856	Kay, William, B.A., 21, Dalhousie-street, Glasgow
Nov.	4, 1869	‖Keightley, W. F., Esq., Old-hall, Milnthorpe, Westmorland
April	4, 1867	‖Kemp, David Skinner, Esq., Bombay
May	18, 1857	Kensington, Edward Thomas, Esq., Beacon Downes, near Exeter
May	4, 1865	Kirkham, Thomas Nesham, Esq., Cambridge Villa, Gilston-road, West Brompton
June	16, 1864	Knox, G. W., Esq., B. Sc., 11, East-parade, Sheffield
Feb.	17, 1859	Kynaston, Josiah W., Esq., St. Helens, Lancashire
Feb.	3, 1859	‖Lackersteen, Mark Henry, M.D., M.R.C.P., F.R.C.S., F.L.S., 28, St. Stephen's-road, Westbourne-park, W.
Feb.	4, 1864	Lambert, Charles, Esq., 3, Queen-street-place, Upper Thames-street, E.C.
Mar.	3, 1859	Lansdell, Mark J., Esq., 38, Gracechurch-street, E.C.
Jan.	20, 1870	Lapper, Edwin, Laboratory, Royal Veterinary College, N.W.
June	17, 1850	‖Lawes, John Bennet, F.R.S., Rothamsted, near St. Albans
May	18, 1857	Leech, Thomas, Esq., 65, Kensington-gardens-square, Hyde-park, W.
Feb.	23, 1841*	‖Leeson, H. B., M.D., F.R.S., Bonchurch, Isle of Wight
Mar.	17, 1859	Letheby, Henry, M.B., 17, Sussex-place, Regent's-park
Nov.	18, 1869	‖Lewis, W. J., Esq., Oriel College, Oxford
June	21, 1866	Lightbown, J. H., Esq., care of R. Lightbown, Pernambuco, Brazil
May	16, 1861	Lindsay, Thomas, Esq., Cooke-street Brewery, Salford, Manchester
Nov.	21, 1853	‖Liveing, G. D., Esq., M.A., Cambridge
Feb.	23, 1841	*Longstaff, George Dixon, M.D., Southfields, Wandsworth, S.W., and 9, Upper Thames-street, E.C.
Dec.	15, 1856	Lowe, Charles, Esq., Smethwick-hall, Brereton, near Congleton, Cheshire
May	3, 1866	Lundy, J. J., Esq., F.G.S., Leith
Dec.	5, 1867	Lunge, Dr. George, 10, Albert-terrace. South Shields
Feb.	3, 1859	‖Lyte, F. Maxwell, Esq., Bagnéres de Bigarre, Hautes Pyrénées, France
Feb.	21, 1853	Macadam, Stevenson, Ph. D., F.R.S.E., Surgeons'-hall, Edinburgh
Dec.	18, 1862	Machattie, A. T., M.D., 1, Stanley-street, Glasgow
April	4, 1867	Mackay, John, Esq., 119, George-street, Edinburgh
Jan.	15, 1844	Maclagan, Douglas, M.D., F.R.S.E., School of Medicine, Surgeons'-hall, and 28, Heriot-row, Edinburgh
April	21, 1864	Mactear, James, Esq., St. Rollox, Glasgow
April	5, 1866	McCalmont, Robert, Esq., Messrs. Ritchie and Sons, Belfast
April	19, 1860	McDonnell, John, Esq., Clare-villa, Rathmines, Dublin
Dec.	17, 1857	McDougall, Alexr., Esq., Barco Lodge, Penrith
Feb.	6, 1868	McLeod, Herbert, Esq., Royal College of Chemistry, Oxford-street, W.
May	1, 1862	Madan, H. G., Esq., Eton College, Windsor
Mar.	17, 1845	Makins, Geo. H., Esq., Danesfield, Walton-on-Thames
Dec.	17, 1857	Mallett, J. W., Ph. D., care of Robert Mallett, Esq., 16, The Grove, Clapham-road, S.W.
Feb.	4, 1858	‖Manning, F. A., Esq., 3, Leadenhall-street, E.C.
Feb.	7, 1853	Marcet, W., M.D., F.R.S., 48, Harley-street, W.

Date of Election.	
Dec. 6, 1866	Marreco, A. F., Esq., Laboratory, College of Medicine, Newcastle-on-Tyne
Nov. 16, 1865	Marriott, William, Esq., Grafton-place, Huddersfield
June 2, 1851	Maskelyne, Nevil Story, Esq., British Museum, W.C.
Nov. 4, 1858	‖Mason, James, Esq., Eynsham Hall, near Witney, Oxon
Jan. 16, 1868	Mason, W. G., Esq., Kennell Hall, Killinghall, Ripley, Yorkshire
Mar. 6, 1862	Mathews, F. C., jun., Esq., Driffield
Feb. 17, 1859	‖Matthews, Henry, Esq., 60, Gower-street, Bedford-square, W.C.
Feb. 18, 1858	‖Matthiessen, A., Ph. D., F.R.S., St. Bartholomew's Hospital, E.C.
Feb. 4, 1850	Maule, G., Esq., 73, Palmerston-buildings, Bishopsgate-street, E.C.
Dec. 7, 1865	‖Maxwell, Theodore, Esq., High Roding Rectory, Dunmow, Essex
Dec. 5, 1867	Maybury, Charles Walter, Esq., 90, King-street, Manchester
Mar. 20, 1862	Mayer, John, Esq., 2, Carlton-place, Glasgow
Dec. 16, 1850	‖Medlock, Henry, Esq., 22, Tavistock-square, W.C.
	Meldrum, Edward, Esq., Dechmont, by Broxburn, near Edinburgh
Jan. 18, 1847	Mercer, John, Esq., Oakenshaw, Blackburn, Lancashire
Feb. 18, 1856	Mercer, Nathan, Esq., Apothecaries' Hall, Montreal
May 6, 1869	Meusel, Dr. E., Laboratory, University College, W.C.
Dec. 4, 1862	Michael, W. H., Esq., Cholmeley-park, Highgate, N.
May 20, 1844	‖Middleton, J., Esq., 79, Cambridge-terrace, Hyde-park, W.
Dec. 18, 1843	‖Millar, James, Esq., William Brown, Esq., 87, St. Vincent-street, Glasgow
Feb. 23, 1841	*Miller, Wm. Hallows, Esq., M.A., F.R.S., Scroope-terrace, Cambridge
June 4, 1868	Miller, F. B., Esq., Royal Mint, Sydney
Dec. 15, 1845	Miller, Wm. Allen, M.D., F.R.S., King's College, W.C., and Upper Tulse-hill, Brixton, S.
Dec. 18, 1862	Mills, E. J., Esq., D. Sc., 12, Pemberton-terrace, St. John's Park-road, N.
Feb. 18, 1864	Morfit, Campbell, Ph. D., Sudbrook Park, Petersham, Surrey
Nov. 4, 1869	Morrison, John, Esq., Arklow Chemical Works, Arklow
Dec. 15, 1851	Morson, Thomas, jun., Esq., 124, Southampton-row, Russell-square, W.C.
May 6, 1869	Muir, J. M., Esq., Assay Office, Bank of Australia
Feb. 3, 1859	‖Müller, Hugo, Ph. D., F.R.S., 110, Bunhill-row, E.C.
Dec. 9, 1869	Murchison, Sir R. I., Bart., F.R.S., Belgrave-square, S.W.
Feb. 20, 1868	‖Murphy, Martin, Esq., College of Chemistry, Duke-street, Liverpool
Dec. 18, 1848	Muspratt, F., Esq., 21, Westmoreland-place, Bayswater, W.
Nov. 4, 1844	‖Muspratt, James Sheridan, M.D., Ph. D., F.R.S.E., Col. of Chemistry, Liverpool
Jan. 15, 1863	Muspratt, J. L., Esq., Widnes, near Warrington
Jan. 21, 1869	‖Muspratt, E. K., Esq., Seaforth Hall, near Liverpool
Dec. 18, 1843	‖Muter, Andrew, Esq., Milton, Dumbartonshire
Dec. 18, 1848	Napier, James, Esq., Netherfield-house, Duke-street, Glasgow
	Neild, Alfred, Esq., Mayfield, Manchester
April 19, 1860	Newlands, J. A. R., Esq., 13, Knowle-road, Brixton, S.W.
Feb. 18, 1864	Newlands, B. E. R., Esq., 4, Malvern-ter., Victoria-road, Charlton, S.E.
May 15, 1848	Nicholson, E. Chambers, Esq., Herne-hill, S.
Feb. 15, 1866	Nickels, Benjamin, Esq., 114, Victoria Park-road, South Hackney
Nov. 6, 1854	Noad, H. M., Ph. D., F.R.S., St. George's Hospital, S.W.
May 6, 1869	Noble, Captain A., Engineer, Elswick Ordnance Works, Newcastle
Jan. 15, 1863	Noble, John, Esq., Royal Arsenal General School, Woolwich, S.E.
April 4, 1861	Norrington, Frederick, Esq., Richmond-villa, Queen's-road, Clifton
Dec. 18, 1854	Norton, Fletcher, Esq., Broderick-street, Middleton, Cork
Jan. 17, 1848	Odling, William, M.B., F.R.S., Croydon, S., and Royal Institution, Albemarle-street, W.
May 6, 1858	O'Neill, Charles, Esq., 4, Bank-place, Salford, Manchester
Nov. 4, 1869	Orme, Temple A., Esq., University College, W.C.
Feb. 7, 1867	Ottley, George, Esq., Carshalton, Surrey
Dec. 15, 1851	Oxland, Robert, Dr., Compton Gifford, near Plymouth

Date of Election.		
Nov. 15, 1866		Page, David, Esq., 44, Gilmore-place, Edinburgh
Nov. 19, 1868	‖	Palmer, Dr. W. J., care of Messrs. Grindlay, 55, Parliament-street, S.W.
Nov. 2, 1865		Parkinson, James, Esq., 4, Gloucester-road, South Kensington
Nov. 1, 1842		Parnell, Edawrd Andrew, Esq., Landore Alkali Works, Swansea
May 20, 1858		Parry, George, Esq., Ebbw Vale Iron, Steel, and Coal Company, Monmouthshire
Dec. 3, 1863		Pattinson, John, Esq., 75, Side, Newcastle-upon-Tyne
Mar. 5, 1868	‖	Paul, Dr. B. H., Analytical Laboratory, 1, Victoria-street, Westminster, W.
Dec. 1, 1864		Payne, J. F., Esq., 4, Kildare-gardens, Bayswater, W.
Feb. 21, 1867		Payne, Martin Henry, Esq., University College, W.C.
Feb. 23, 1841	‖*	Pearsall, Thomas, F.R.S.E., Mechanics' Institution, Southampton-buildings, Holborn, W.C.
Feb. 4, 1870		Pedlar, Alexander, 12, Wood-lane, Forest-hill, S.E.
Jan. 21, 1864		Pentecost, John, Esq., Beaumont, Wordsley, Stourbridge
April 4, 1843		Pepper, John Henry, Esq., 61, Boundary-road, St. John's-wood, N.W.
Feb. 2, 1865		Percival, Richard, Esq., The Shrubbery, Bexley Heath, Kent
Dec. 15, 1856	‖	Perkin, W. H., F.R.S., Seymour-villa, Sudbury, Middlesex
Mar. 6, 1862	‖	Perrins, J. D., Esq., Davenham-Bank, Malvern
May 2, 1867		Peterson, F. W., Esq., H.M. Mint, Calcutta
Mar. 15, 1866		Phillips, C. P., Esq., 109, Fenchurch-street, E.C.
Jan. 18, 1842		Phillips, J. Arthur, Esq., Cressington-park, Aigburth, Liverpool
Jan. 16, 1862		Phipson, T. L., Ph. D., 4, Cedars, Putney
Dec. 4, 1862		Piesse, G. W. S., Esq., Ph. D., 2, New Bond-street, W.
Nov. 15, 1860	‖	Player, J. H., Esq., 111, Hagley-road, Edgbaston, near Birmingham
Feb. 23, 1841	‖*	Playfair, Lyon, C.B., F.R.S., 4, Queensbury-place, South Kensington
Jan. 19, 1860		Plunket, Wm, Esq., Royal College of Science, Stephen's-green, Dublin
April 1, 1858		Pochin, Henry Davis, Esq., Barn Elms, Barnes, Surrey
Mar. 21, 1853		Pollock, Henry, Esq., 18, Hanover-terrace, Regent's-park, N.W.
Dec. 4, 1848		Pontifex, Edmund A., Esq., 15A, Cleveland-square, Bayswater, W.
June 16, 1864		Pontifex, S. R., Esq., George Town, Demerara.
Mar. 6, 1862		Pooley, T. A., Esq., Southside, Clapham Common, S.W.
Feb. 17, 1870		Prangley, Arthur Redland, Presht.
May 5, 1864		Prentice, E. H., Esq., Stowmarket, Suffolk
May 19, 1864	‖	Prentice, Manning, Esq., Violet-hill, Stowmarket
May 16, 1861		Prestwich, Joseph, Esq., F.R.S., Shorcham, near Sevenoaks
Mar. 3, 1851		Price, Astley Paston, Ph. D., 47, Lincoln's-inn-fields, W.C.
June 3, 1850		Price, David Simpson, Ph. D., 26, Great George-street, Westminster
Feb. 17, 1870		Pritchard, William, Royal Veterinary College, Camden-town, N.W.
May 3, 1860		Procter, William. M.D., 24, Peter-gate, York
Feb. 1, 1866		Purser, Edward, jun., Esq., 116, Fenchurch-street, E.C.
April 18, 1843		Randall, William B., Esq., Basset, Southampton
Jan. 16, 1862		Raynor, H., Esq., Smethwick, near Birmingham
Nov. 7, 1843		Redwood, Theophilus, Ph. D., Pharmaceutical Society, Bloomsbury-square, W.C., and Earlscroft, Lower Clapton-road
Jan. 18, 1866		Redwood, T. B., Esq., Earlscroft, Lower Clapton-road
Feb. 2, 1865		Reid, John, Esq., The Place, Monswald, Dumfriesshire
May 6, 1869		Reinold, A. W., Esq., Clifton College, Bristol
		Reynolds, Colonel, J. W., Army and Navy Club, St. James'-square, S.W.
Nov. 19, 1857		Reynolds, Richard, Esq., 13, Briggate, Leeds
Dec. 4, 1862		Richard, James, Esq., Clifton-lodge, near Preston, Lancashire
April 19, 1866		Richardson, Joseph, jun., Esq., 16, Dawson-street, Manchester
Dec. 1, 1864		Richardson, J. G. F., Esq., Houghton House, Stoney-gate, Leicester
Feb. 3, 1845	‖	Rickard, W. T., Esq., 6, Clyde-terrace, Grove-road, Mile-end, E.
June 18, 1868		Riddel, H. B., Esq., 41, Rutland-gate, Knightsbridge
Dec. 15, 1851		Riley, Edward, Esq., 31, Park-square, Leeds
Dec. 7, 1865		Ritchie, W. B., Esq., Mount Pottinger, Belfast
Mar. 3, 1864		Ritchie, William, jun., Esq., Kincaid-field House, Milton of Campsie, Glasgow

Date of Election.	
Nov. 7, 1866	Roberts, William Chandler, Esq., Royal Mint, E.
April 6, 1865	‖Robertson, George B., Esq., Inland Revenue, Somerset House, W.C.
May 3, 1866	Robinson, John, Esq., Oxford
Dec. 4, 1862	Rodwell, G. F., Esq., 14, Denbigh-place, Belgrave-road, S.W.
	Ronalds, Edmund, Ph. D., Bonuington House, Bonnington, Edinburgh
Dec. 17, 1855	Roscoe, H. E., Ph. D., F.R.S., Owen's College, Manchester
Feb. 17, 1870	Ross, Lewis Buttle, Driffield
Feb. 18, 1869	Rossiter, William, Esq., South London College, 91, Blackfriars-road, S.E., and White Hill House, Frimley
Dec. 1, 1864	Rouch, W. W., Esq., 180, Strand, W.C.
Nov. 2, 1865	Row, Frederic, Esq., High-street, Braintree
Dec. 17, 1868	Rowan, Thomas, Esq., North Woodside House, Glasgow
Mar. 21, 1848	Rowney, Thomas H., Ph. D., Queen's College, Galway
Mar. 20, 1862	Royle, Thomas, Esq., Crayford, S.E.
Jan. 21, 1858	Rumney Robert, Esq., Ardwick Chemical Works, Manchester
Mar. 3, 1851	‖Russell, W. J., Ph. D., 34, Upper Hamilton-ter., St. John's-wood, N.W.
	‖Rylands, Thomas Glazebrook, Esq., F.L.S., Heath-house, Warrington
June 18, 1868	Sadler, S. A., Esq., Oldbury, Birmingham
April 16, 1863	‖Salt, Henry, Esq., 29, Gordon-square, W.C.
Feb. 17, 1859	‖Salter, Thomas, W., Esq., St. John's-cottage, Battersea-rise
Nov. 6, 1854	Samuelson, Newton, Esq., 9, Hackins Hey, Liverpool
Feb. 6, 1868	Schenk, Dr., 10, Hanover-place, Kennington-park, W.
Mar. 15, 1842	Schunck, Edward, Ph. D., F.R.S., Oaklands, Kersall, Manchester
May 17, 1842	Schweitzer, Edward G., Esq., 26, Westbourne-park, W.
June 18, 1863	Scorgie, James, Esq., Free General Assembly's Institution, Bombay
Dec. 17, 1863	Scotson, James, Esq., Chester Bank, Prestwich, Manchester
Dec. 1, 1864	Scott, Colonel H. Y. D., R.E., Ealing, W.
Jan. 20, 1870	Seward, Henry, 15, Barnsbury-park, London, N.
Dec. 15, 1859	Sibson, Alfred, Esq., 11, Eaton-terrace, St. John's-wood, N.W.
	Simpson, Maxwell, M.B., F.R.S., 11, Alexander-street, Bayswater
Mar. 15, 1852	Smee, Alfred, F.R.S., 7, Finsbury-circus, E.C.
Feb. 5, 1863	Smee, Alfred, jun., Esq., 7, Finsbury-circus, E.C.
Feb. 2, 1865	Smith, Arthur, Esq., Pera Lodge, Loughborough-road, Brixton, S.
Feb. 23, 1841	*Smith, J. Denham, Esq., Kenton-lodge, Middlesex, N.W.
April 7, 1856	Smith, Thomas J., F.G.S., Hessle, near Hull, and 10, North Church-side, Hull
Jan. 16, 1854	Smith, H. J., B.A., F.R.S., 20, Devonshire-street, Oxford
Feb. 3, 1845	Smith, Robert Angus, Ph. D., F.R.S., 20, Devonshire-street, Manchester
Dec. 6, 1852	‖Smith, John, M.D., Sydney
Jan. 18, 1866	Smith, R. H., Esq., 329, Glossop-road, Sheffield
Dec. 20, 1866	Smith, Watson, jun., Esq., 26, Hawthorn House, Wilmslow, Cheshire
Dec. 19, 1867	Smith, Dr. Frank, 79, Norfolk-street, Sheffield
Dec. 9, 1869	Smith, Edward, Esq., Strand, Torquay
June 21, 1866	Sparks, E. I., Esq., Crewkerne, Somerset
Jan. 18, 1866	Speir, James, Esq., Messrs. Barclay and Speir, Newcastle-on-Tyne
Dec. 1, 1864	Spence, J. B., Esq., Newton-heath, near Manchester
May 1, 1862	Spence, Peter, Esq., Pendleton Alum Works, Newton-heath, Manchester
April 7, 1851	Spencer, Thomas, Esq., 32, Euston-square, N.W.
Feb. 3, 1859	Spiller, John, Esq., 35, Grosvenor-road, Highbury New Park, London, N.
Jan. 15, 1863	‖Spiller, William, Esq., Atlas Dye Works, Hackney-wick, N.E.
Dec. 1, 1864	Sprengel, Hermann, Ph. D., 79, Gloucester-street, Pimlico, S.W.
Feb. 4, 1858	Squire, W. Stevens, Ph. D., 37, Accacia-road, Regent's-park.
April 21, 1859	‖Stanford, Edward Charles, Esq., Edinbarnet, by Dantocher, Dumbartonshire
Mar. 17, 1864	Staples, B. C., Esq., Sydenham-road North, Croydon, S.
April 19, 1860	Stark, M. J., Esq., Norwich
Feb. 23, 1841	*Stenhouse, John, LL.D., F.R.S., 17, Rodney-street, Pentonville, N.
April 5, 1866	Stevens, William Carr, Esq., 33, Mark-lane, E.C.

Date of Election.	
Dec. 20, 1847	Stevenson, James C., Esq , Jarrow Chemical Works, South Shields
Feb. 18, 1864	Stevenson, Thomas, M.D., Guy's Hospital, S.E
Dec. 15, 1864	Stewart, A. Y., Esq., Apothecaries'-hall, Blackfriars, E.C.
Mar. 7, 1867	Stewart, Major, R. C., Deputy Assistant Adj.-General, Horse Guards, and 12, Prince of Wales's-terrace, Kensington-palace, W.
June 21, 1866	Stock, W. F. K., Esq., Elm-bank, Darlington, Durham
Dec. 17, 1868	Stoddart, W. Walter, Esq., Laboratory, 9, North-street, Bristol
May 19, 1851	Stone, Daniel, Esq., Royal School of Medicine, Faulkner-street, Manchester
Jan. 16, 1862	Storey, J., Esq., Messrs. Storey, Bros., Lancaster
May 4, 1865	Sugden, Joseph, jun., Esq., Trinity-house, Halifax
April 19, 1860	Sutton, F., Esq., Laboratory, Bank Plain, Norwich
June 15, 1865	Sweeting, G. B., Esq., King's Lynn, Norfolk
April 3, 1862	Symons, William, Esq., 26, Joy-street, Barnstaple, Devon
Dec. 1, 1864	Tarner, Alfred Pythian, Esq., 97, High-street, Marylebone, W.
Dec. 5, 1867	Tatlock, Robert R., Esq., Assay Office, George-street, Glasgow
Nov. 6, 1854	Taylor, Jas., Esq., Farmers' Club, Salisbury-square, Fleet-street, E.C.
Mar. 16, 1846	Taylor, Thomas, Esq., Lecturer on Chemistry, Middlesex Hospital, Warwick House, Warwick-place, Grove End-road, N.W.
June 1, 1841	Tennant, James, Esq., 149, Strand, W.C.
May 5, 1864	Teschemacher, E. F., Esq., 1, Highbury-park North
April 15, 1858	Thomas, T., Begbrook, Frenchay, Bristol
Nov. 17, 1859	Thomas, Andrew, Esq., 13, Hendley-street, Adelaide, South Australia
Jan. 16, 1862	Thomas, R. W., Esq., 10, Pall Mall, S.W.
Feb. 5, 1863	Thompson, R. E., M.D., 21, South-street, Park-lane, W.
Dec. 20, 1866	Thomson, Dr. A. M., 166, Upper-street, Islington, N.
April 15, 1858	Thomson, John, Esq , 7, Lower Kennington-lane, S.
Mar. 4, 1858	Thornthwaite, William, Esq., 123, Newgate-street, E.C.
Feb. 1, 1866	Thorp, William, jun., Esq., 39, Sandringham-road, West Hackney, N.E.
Dec. 20, 1860	Thudicum, John L. W., M.D., 3, Pembroke-road, Kensington, W.
Feb. 19, 1863	Tichborne, C. R. C., Esq., Apothecaries' Hall of Ireland, Dublin
Dec. 5, 1867	Tidy, Dr. C. M., The Hollies, Cambridge-heath, Hackney, N.E.
June 1, 1865	Tilden, W. A., Esq., 17, Bloomsbury-square, W.C.
June 20, 1853	Tomlin, Andrew, Esq., Valparaiso
June 2, 1864	Tomlinson, Charles, Esq , F.R.S., Highgate, N.
Jan. 15, 1855	Tookey, Charles, Esq., Museum of Practical Geology, Jermyn-street, S.W.
Dec. 3, 1868	Tosh, Dr. E. J., Laboratory, Whitehaven
Mar. 21, 1867	Tribe, Alfred, Esq., 73, Artesian-road, Bayswater, W.
Nov. 3, 1856	Tuson, Richard V., Esq., Royal Veterinary College, Camden-town, N.W.
April 2, 1868	Tyndall, Dr. John, F.R.S., Royal Institution, Albemarle-street, W.
Nov. 16, 1865	Umney, Charles, Esq., 40, Aldersgate-street, E.C.
May 18, 1865	Upward, Alfred, Esq., Chartered Gas Works, 146, Goswell-street, E.C.
Feb. 2, 1865	Vacher, Arthur, Esq., 20, Great Marlborough-street, W.
June 3, 1869	Valentin, L. W., Esq., 126, Lancaster-road, Notting Hill, W.
Nov. 7, 1866	Vaughan, E. P. H., Esq., 54, Chancery-lane, W.C.
May 18, 1857	Versmann, Frederick, Dr., 10, Hanway-street, Oxford-street
Dec. 17, 1849	Voelcker, J. A., Ph. D., 39, Argyle-road, Kensington, W.
April 17, 1862	Von Bose, C. Moritz, Esq., Messrs. Gehe and Co., Chemical Works, Dresden
April 5, 1866	Vosper, Thomas, Esq., 27, Nightingale-street, Strangeways, Manchester
Feb. 21, 1867	Waite, William Thurston, Esq., Medical College, London Hospital, E.
Dec. 18, 1843	Waldie, David, Esq., Calcutta
Feb. 15, 1866	Walenn, W. H., Esq., 74, Brecknock-road, N.
Feb. 2, 1865	Walker, J. F., Esq., 16, Gilly-gate, York, and Sidney College, Cambridge
Jan. 16, 1868	Walker, Captain Alexander, R.A., Commissary of Ordnance, Allahabad, India

Date of Election.	
Dec. 15, 1856	Wallace, William, Esq., Ph. D., F.R.S.E., Mechanics' Institution, 38, Bath-street, Glasgow
Dec. 9, 1869	Walton, Thomas, Esq., 3, Bourne-street, Hull
Feb. 19, 1863	Wanklyn, James A., Esq., London Institution, Finsbury-circus, E.C.
April 21, 1864	Ward, George, Esq., Laboratory, Mechanics' Institution and Literary Society, Leeds
Dec. 21, 1865	Ward, Thomas, Esq., Arnold Villas, South Shore, Blackpool
Jan. 6, 1845	Ward, William Sykes, Esq , Denison-hall, Leeds
Mar. 19, 1863	Warington, George, Esq., 1, Conduit-vale, Greenwich, S.E.
Mar. 19, 1863	Warington, Robert, Esq., Atlas Chemical Works, Millwall, E.
Dec. 3, 1857	Watson, Henry Hough, Esq., The Folds, Bolton-le-Moors
Feb. 4 1858	Watson, J. Forbes, M.A., M.D., India Museum, India Office, S.W.
Dec. 20, 1847	Watts, Henry, Esq., B.A., F.R.S., 151, King Henry's-road, South Hampstead, N.W.
April 19, 1866	Watts, W. M., Esq., Beechfield, Bowdon, near Manchester
April 20, 1846	Way, John Thomas, Esq., 9, Russell-road, Kensington, W.
Mar. 1, 1866	Webster, George W., Esq., 33, Bridge-street, Warrington
Feb. 21, 1861	Weston, William, Esq., Chemical Department, Portsmouth Dockyard
Feb. 23, 1841	*Wheeler, James Lowe, Esq., Lionel-villa, Overton-road, Angel-town, Brixton, S.
June 2, 1851	Whipple, George, Esq , 10, Mortimer-road, De Beauvoir-square, Kingsland, N.
	White, Alfred, F.L.S., West Drayton
Mar. 20, 1862	White, Leedham, Esq., 17, Millbank-street, Westminster, S.W.
Mar. 5, 1868	White, T. W., Esq., Ifield, near Crawley, Sussex
Nov. 5, 1863	Whitfield, John, Esq., 18, Westbro', Scarborough
Dec. 9, 1869	Wiggon, John, Esq., 34, St. Matthew's, Ipswich
June 17, 1858	Williams, John, Esq., 5, New Cavendish-street, W.
May 18, 1857	Williams, William M., Esq., The Laboratory, Atlas Works, Sheffield
Jan. 16, 1862	Williams, C. Greville, Esq., F.R.S., 4, Oxford-road, Turnham Green, W.
Jan. 21, 1869	Williams, Rev. Stephen, Stonyhurst College, Blackburn
May 15, 1848	Williamson, A. W., Ph. D., F.R.S., University College, W.C.
Feb. 17, 1870	Wills, Thomas, Royal Institution, Albemarle-street, W.
June 7, 1866	Wilson, C., Esq., Bridgwater Smelting Company, St. Helens, Lancashire
Nov. 19, 1855	Wilson, G. F., Esq., F.R.S., East Hill, Wandsworth, S.W.
Dec. 4, 1862	Wilson, J. C., Esq., School of Medicine, Leeds
May 3, 1852	Wilson, William, Esq., Jubilee-street, Mile-end, E.
Mar. 2, 1857	Winstone, Benjamin, M.D., 7, Ely-place, E.C.
May 7, 1863	Wood, Thomas, Ph. D., 23, Grove-street, Alpha-road, N.W.
Dec. 5, 1867	Wood, Augustus A., Esq., 74, Cheapside, E.C.
Jan. 19, 1860	Wood, Charles Henry, Esq., 25, Devonshire-road, Seven Sisters'-road, N.
Feb. 4, 1858	Worsley, Philip, J., Esq., 1, Codrington-place, Clifton, Bristol
June 7, 1866	Wright, Charles, R. A., Esq., Laboratory, Washington Chemical Company, Washington, county Durham
Feb. 17, 1870	Wright, Philip, The Elms, Ripley, Derbyshire.
May 16, 1861	Wright, W. C., Esq., 46, Mosley-street, Manchester
Feb. 4, 1864	Wrightson, John, Esq., Royal Agricultural College, Cirencester
May 19. 1864	Wrightson, Francis, Ph. D., Nine Elms, King's Norton, near Birmingham
Feb. 2, 1865	Wyndham, Heathcote, Esq., Oriel College, Oxford
Feb. 23, 1841	*Yorke, Colonel Philip, F.R.S., 89, Eaton-place, Belgrave-square, S.W.
	Young, James, Esq., Limefield, West Calder, Midlothian

ASSOCIATES.

Mar. 19, 1861	Meuzel, Dr.
	Richter, Reinhold, Esq., Harpenden, near St. Albans
Nov. 4, 1869	Gerstl, Mr.

FOREIGN MEMBERS.

NUMBER NOT TO EXCEED FORTY.

Date of Election.	
Jan. 20, 1851	Balard, A. J., Collége de France, Paris
Mar. 1, 1860	Berthelot, M., Collége de France, Paris
June 18, 1849	Boussingault, J. B., Paris
Feb. 1, 1842	Bunsen, R. W., Ph. D., F.R.S., University of Heidelberg
May 18, 1858	Cahours, Auguste, à la Monnaie, Paris
June 19, 1862	Canizzaro, S., University of Palermo
June 18, 1849	Chevreul, Michel Eugène, F.R.S., Jardin des Plantes, Paris
April 21, 1864	Dessaignes, Victor, M.D., Vendôme, Dep. Loire-et-Cher, France
Mar. 1, 1860	Deville, Henri Sainte Claire, Ecole Normale, Paris
Dec. 6, 1847	Dumas, Jean Baptiste, F.R.S., Paris
April 21, 1864	Fehling, Hermann von, Ph. D., Stuttgart
Mar. 1, 1860	Fremy, Edmond, Ecole Polytechnique, Paris
Nov. 4, 1844	Fresenius, C. Remigius, Ph. D., Wiesbaden
Mar. 1, 1860	Fritzsche, J., St. Petersburgh
May 3, 1866	Gibbs, Professor Wolcott, Cambridge, Massachussets, U.S.
June 19, 1862	Kekulé, A., Ph. D., University of Bonn
May 17, 1847	Kolbe, Hermann, Ph. D., University of Leipzig
June 18, 1849	Kopp, Hermann, Ph. D., University of Heidelberg
June 1, 1841	Liebig, Baron Justus von, F.R.S., University of Munich
June 19, 1862	Loewig, C., Ph. D., University of Breslau
	Magnus, Gustav., F.R.S., University of Berlin
June 19, 1862	Malaguti, Rennes, Brittany
June 19, 1862	Marignac, Jean Charles, Geneva
Mar. 1, 1860	Mulder, G. J., Bennekom, près de Wageningen, Pays-Bas
June 19, 1862	Pasteur, L., F.R.S., Ecole Normale, Paris
Mar. 1, 1860	Peligot, E., à la Monnaie, Paris
May 3, 1866	Rammelsberg, Professor, Berlin
Mar. 15, 1842	Redtenbacher, Joseph, Ph. D., University of Vienna
June 18, 1849	Regnault, Henri Victor, F.R.S., Paris
	Schrötter, Ritter v. Cristelli, Director des Münzamts, Vienna
June 19, 1862	Stas, J. S., Ecole Militaire, Brussels
	Strecker, Adolph, Ph. D., University of Tübingen
May 3, 1866	Weltzien, Professor, Carlsruhe
April 18, 1843	Will, Heinrich, Ph. D., University of Giessen
June 18, 1849	Wöhler, F., F.R.S., University of Göttingen
	Wurtz, Adolphe, F.R.S., Ecole de Medicine, Paris
June 19, 1862	Zinin, Nicolaus, St. Petersburgh

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